

## **TEXTURAL AND CHEMICAL CHARACTERISATION OF ACTIVATED CARBONS PREPARED FROM RICE HUSK (ORYZA SATIVA) USING A TWO- STAGE ACTIVATION PROCESS**

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### **Abstract**

Activated carbons from agro-industrial wastes; rice husk; were prepared by physical and chemical activation using phosphoric acid as the dehydrating agent. A two-stage activation process method was used; with semi-carbonisation stage at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression as reported in the literature. All experiments were conducted in a laboratory scale muffle furnace under static conditions in a self generated atmosphere covering process parameters such as impregnation ratios. We found that by using this method, the AC5 had the highest iodine number and methylene blue adsorption capacity which was 506.6 mg/g and 319.0 mg/g respectively.

Keywords: Activated Carbons, Two-Stage Activation Process, Physical, Chemical Properties

### **1. Introduction**

Activated carbon materials have been applied most frequently as adsorbents and virtually displaced other materials in water purification, solvent recovery, gas refining, air purification, exhaust desulphurisation, deodorisation, metal ion separation and recovery [1, 2] and leachate treatment [3-5]. This material can be designed for adsorption of specific adsorbate, by using appropriate precursor [1-8], dehydrating agent and by optimizing the activation process conditions. Several

activating agents have been reported for chemical activation process; however the most important and commonly used activating agents are zinc chloride, potassium hydroxide and alkaline metals. This agent, which has dehydrating properties, will influence the pyrolytic decomposition and retard the formation of tars during the carbonization process, increasing the carbon yield [9]. A number of activation methods have been reported in the literature using  $H_3PO_4$  as an activating agent. The chemical nature of activated carbon significantly influences its adsorptive, electrochemical, catalytic, and other properties. However, few papers report on the effects on chemical preparation conditions and preparation methods on the carbon. Generally, activation methods can be classified as single-stage or two-stage activation process carried out either in inert medium or a self-generated atmosphere as shown in Table 1. This paper explains the effect of  $H_3PO_4$  impregnation to the precursors prepared by using a two-stage activation process method in a self-generated atmosphere. Trial and error methods were employed to achieve a high surface area carbon with desired pore size by optimizing the process parameters such as the activation time, activation temperature and impregnation ratio. Table 1 summarizes efforts by researchers to prepare activated carbons using  $H_3PO_4$  activation with reference to the precursors, experiment conditions and results.

Generally, it is possible to categorise the different experimental methods with different precursors as follows:

1. Impregnation of precursors and drying, followed by activation at different temperature for different activation time in self-generated or inert atmosphere [10].
2. Impregnation of precursors, then semi-carbonisation followed by activation at specific temperature in self-generated or inert atmosphere for a specific length of time [11, 12].
3. Precursors are directly activated and then impregnated at desired temperature in self-generated or inert atmosphere for a specific length of time [13].
4. Precursors are carbonized, then impregnated, followed by activation at a specific length of time. This is a three-stage process [14].
5. A dilute mixture of precursor and dehydrating agent is activated in a liquid-phase carbonization step, followed by air activation and then by secondary air activation. This is also known as a three-stage process [15].

Category 2 was chosen due to the simplicity and cost factor for the production and study of activated carbons prepared from rice husk.

## 2. Experimental Procedures

The rice husks used in this study were obtained from Kampung Rukom, Pitas in Kota Marudu, Sabah. The species of the rice is *oryza sativa* and is locally known as *Padi Ininduruk*. Prior to the impregnation process, the precursors were washed with distilled water and dried in an oven at  $110^\circ\text{C}$  for 24 hours and ground to 0.5–2.0 mm in size. This was done to remove sand, branch fibers and dirt from contaminating the samples as explained in our previous papers [1, 2, 6, 7]. Impregnation process was done using  $H_3PO_4$  as the dehydrating agent. 0 – 12 M of  $H_3PO_4$  solutions were placed separately into Erlenmeyer flask (250 ml) as shown in Table 2. The flask was then placed in an orbital shaker model 721 Protech for a week. The samples were dried overnight in an oven at  $110^\circ\text{C}$ . A

muffle furnace model Carbolite RHF 1500 was used to semi-carbonized the samples at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression methods as described in earlier works [1, 2, 6, 7, 12, 14, 16-18]. After that, the activated carbons were refluxed in distilled water except for ACPHY which was reflux in an acid solution (0.1M HNO<sub>3</sub>) to remove metals ions, tar and ash followed by distilled water (10 times) to remove the acid. The activated carbons were dried in an oven at 110°C for a week, after which, yield percentage, pH [19], scanning electronic microscopy, iodine number and methylene blue adsorption capacity of the selected activated carbon were determined.

**Table 1. Summary of Earlier Work by Researchers to Prepare Activated Carbons Using H<sub>3</sub>PO<sub>4</sub> Activation.**

Researcher	Precursor	Experimental Condition	Results
Kirubakaran et al. [10]	Coconut Shell	Two stage in N <sub>2</sub> atm; A.T=400 to 600°C; A.time=2 hr.	S.A > 1000 m <sup>2</sup> /g at I.R=1.5
Toles et al. [20]	Macadamia shell, pecan, walnut and almond	Single and two stage; N <sub>2</sub> and self-generated atm.; S.C.T.=170°C; S.C. time=30min.; A.T.=450°C; A. time=1h	S.A=1100 to 1600 m <sup>2</sup> /g. Activation in self-generated atm gave the highest S.A.
Dastgheib and Rockstraw [15]	Pecan Shells	Three stage activation: 1) liquid-stage activation at 160°C 2) primary activation at 160-210°C 3) secondary activation at 300-500°C for 30 min, I.R.=3	S.A=1071 m <sup>2</sup> /g. S.A. increases until secondary A.T of 450°C and reduces when temperature increases above 450°C.
Lafi [13]	Acorns and olive seeds	A single stage with self-generated atmosphere. A.T=400-800°C. A.time=1 h.	A.T=800°C produced the highest Methylene Blue no. of 130 mg/g
Ahmedna [11, 12]	Sugarcane bagasse	Two stage with N <sub>2</sub> atmosphere. A.T=450°C. A.time=1 h.	S.A=1200 m <sup>2</sup> /g

S.A =surface area; S.C.T=semi-carbonization temperature; S.C. time=semi-carbonization time; A.T=activation temperature; A. time=activation time; I.R. impregnation ratio.

### 3. Results and Discussion

Temperature, heating period, materials, dehydrating agent and the method of carbonization and activation play an important role in determining the properties of the resulting activated carbon. Previous work in our laboratories [1, 2, 6, 7] suggested that the temperature played an important role to produce optimum surface area for the carbons.

#### 3.1. Chemical activation

Although this is a two-stage activation process, the action of phosphoric acid in the activation of the rice husk may be visualized as to take place in three stages in the process of preparation, that is impregnation, pyrolysis in self-generated atmosphere and final leaching of the impregnant using distilled water. During the course of soaking, the acid introduced into the lignocellulose produces chemical changes and structural alterations, involving dehydration and redistribution of biopolymers causing linkages between the lignin and cellulose creating a rigid cross linked solid. The subsequent physical and chemical changes modified the thermal degradation process. As a consequence, the temperature of the process does not need to be high. During impregnation, there is a weakening of the precursor structure, a hydrolysis reaction (with loss of volatile matter) an increase in elasticity and swelling of the particle. These phenomena were intensified with the increasing amount of chemical introduced into the precursor.

This explains the increment pattern in the percentage of yield as the impregnation ratios increases as shown in Table 2. This pattern was observed even after the washing process to remove the phosphoric acid was completed. After impregnation by the phosphoric acid, the rice husk turns black which turns into a dry powder, however, no major change in the physical appearance was observed in the ACPHY. The higher concentration of phosphoric acid produces the smoother powdered form, wet and sticky precursor due to its affinity to moisture. pH was controlled to be within the range of ~5 to 7.

#### 3.2. Carbonisation and activation

Carbonisation is one of the most important steps in the production process of activated carbons since it is in the course of carbonization that the initial porous structure was formed. This stage consist of primary pyrolysis in self-generated atmosphere carried out at 200°C for 15 minutes to remove the excess of lower boiling fraction of the binding agent and the evolution of most gasses with formation of the basic structure of the char. The second stage or activation is done by heating precursor at temperatures up to 500°C for 45 minutes. During the first stage, the impregnated precursor material and the physically activated carbon were found to blacken and formed a plastic mass, which ultimately transforms to a dry char. The completion of the first stage of activation is identified by the transformation of the pasty mass into a dry char. The furnace temperature was first raised at a particular rate until it reaches 500°C before start the second stage of activation. The second stage is consolidation of char structure with a very small weight loss. The increasing impregnation ratio implies a porous development to the precursor.

**Table 2. The Effect of H<sub>3</sub>PO<sub>4</sub> Impregnations (M) on the Percentage of Yield, pH, Iodine Number and Methylene Blue Adsorption Capacity of the Rice Husk Activated Carbons.**

Sample	H <sub>3</sub> PO <sub>4</sub> (M)	% of yield	pH	Iodine Adsorption Capacity (mg/g)	Methylene Blue Adsorption Capacity (mg/g)
Physically activated carbon (ACPHY)	0	40.5	6.47	264.4	220.4
Chemically activated carbon (AC1)	2	67.2	5.67	346.9	227.3
Chemically activated carbon (AC2)	4	72.4	5.51	363.0	242.8
Chemically activated carbon (AC3)	7	75.3	5.30	402.1	300.4
Chemically activated carbon (AC4)	10	78.4	4.83	426.0	310.3
Chemically activated carbon (AC5)	12	79.0	4.77	506.6	319.0

### 3.3. Adsorption studies: Iodine number analysis

It has been established that the iodine number (in mg/g) gives an estimate of the surface area (in m<sup>2</sup>/g) [9], and it measures the porosity for pores with dimensions between 1.0-1.5 nm. The removal of iodine by the activated carbons obtained from phosphoric acid impregnation is related to their porosity characteristics which determine the degree of accessibility of these molecules. A lower adsorption of iodine can be ascribed to the presence of pores narrower than 1.0 nm, which largely makes up most of the structure of these carbons [21]. For precursors impregnated by 2 M phosphoric acid, the mass of iodine absorbed was generally low (346.9 mg/g), whereas carbons produced from 12 M phosphoric acid exhibit a much higher capacity (506.6 mg/g) indicating considerable ultra-microporosity. These carbons contain mostly micropores with a small contribution of mesoporosity. Table 2 shows the mass of iodine absorbed by the activated carbons. An anomalous behavior was observed for the physically activated carbon which gave the lowest up-take of 264.4 mg/g. This value might suggest a low adsorptive process, and is probably associated with a low amount of porosity.

### 3.4. Adsorption studies: Methylene blue adsorptive capacity

The fairly large molecules of methylene blue were also used to study the adsorptive capacity of the activated carbons prepared. In the present investigation, the amount of methylene blue adsorbed, increased with concentration of impregnating agent as shown in Table 2. For carbons impregnated by 2 M phosphoric acid, the mass of methylene blue absorbed was generally low (220.4 mg/g), whereas carbons produced from 12 M phosphoric acid exhibited a much higher capacity (319.0 mg/g) indicating high absorption capacity. These readings correspond with the iodine number data in Table 2.

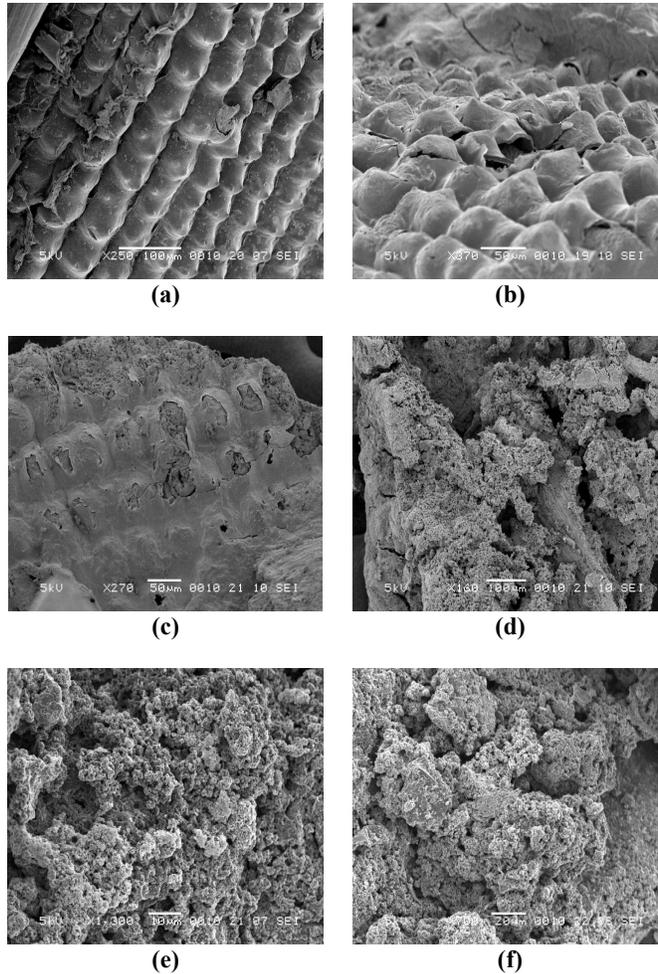
### 3.5. Scanning electron microscopy

Surface morphology carried out on the samples of rice husk based activated carbon after activation using JEOL JSM-5610LV scanning electron microscope showed interesting developments and characteristics. The carbon samples were coated with platinum by a JEOL JFC-1600 Auto Fine Coater for a clear visibility of the surface morphology. The average amount of pores is dependent mainly on the concentration of chemical impregnation [21]. Chemical activation with  $H_3PO_4$  of activated carbons leads to mesoporous carbons at high impregnation ratios. In the present case, the impregnation ratios seem to determine the porosity to a larger degree than activation conditions. The morphology of pore was observed to increase with impregnation ratio as shown in Fig. 1. Progressive development of porosity, especially of larger pores, appears to occur as more acid is incorporated into the precursor. The activated carbon obtained from physical activation characterized by the lowest pore amount as shown in Fig. 1(a) present smooth surfaces. As the impregnation ratio is increase to 2 M  $H_3PO_4$  a generalization of pores of the activated carbons occurs, and agglomerates of pores are produced as shown in Fig. 1(b). This becomes more evident for an impregnation ratio of 7 M  $H_3PO_4$  as shown in Fig. 1(d), where the increase in micropore and mesopore volumes based on data from iodine number and methylene blue adsorptive capacity, suggesting that the formation of additional pores and widening of the existing micropores is the favoured mechanism during  $H_3PO_4$  activation. The higher impregnation ratio produced higher amounts of pores as in Fig. 1(e). The higher impregnation ratio yielded carbons of larger proportion of mesopores. More agglomerates of pores are present in AC5 as shown in Fig. 1(f). This was because AC5 was impregnated by the highest impregnation ratio. AC5 is preferable to be a high quality activated carbon. Therefore, increasing the impregnation ratio is beneficial to the porosity development.

## 4. Conclusions

Production of activated carbon derived from rice husks had been demonstrated to be feasible. High surface area activated carbons were obtained by chemical activation of rice husks with  $H_3PO_4$  and two step activation which was carried out in a self-generated atmosphere. This study showed that the use of dehydrating agent and the two-step activation process in self-generated atmosphere played a major role in shaping and transforming precursors into activated carbons.

Phosphoric acid was used as a dehydrating agent, produced a very different activated carbon, changing not only the pore structure and morphology of the activated carbon but also giving the sponge-like physical appearance of the precursor itself. It is our opinion that impregnating agent coupled with the activation temperature of 500°C contributed to this change.



**Fig. 1. Electron Micrographs of the Physically, (a) ACPHY and Chemically Activated Carbons, (b) AC1, (c) AC2, (d) AC3, (e) AC4, (f) AC5.**

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