



# Synthesis and characterization of mesoporous activated carbon from rice husk for adsorption of glycine from alcohol-aqueous mixture

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## ABSTRACT

Activated carbon prepared from rice husk using phosphoric acid activation has been studied by chemical activation. The surface area, pore volume, and pore size distribution of carbon samples activated at 700, 800, and 900 °C (MAC<sub>700</sub>, MAC<sub>800</sub> and MAC<sub>900</sub>) were measured. Temperature 800 °C was found to be optimum for the increase production of pore volume especially mesopore volume. Hence detailed characterization of MAC<sub>800</sub> was carried out. The X-ray diffraction curve of MAC<sub>800</sub> revealed the evolution of crystallites of carbon and silica during activation at higher temperature. The FTIR spectrum also provided evidence for the presence of silica in the carbon composite. Batch adsorption of glycine onto MAC<sub>800</sub> was carried out. The effect of time, temperature and initial concentration of glycine on the adsorption was studied. pH 6 was found to be optimum for adsorption reaction and the reaction was endothermic in nature. Adsorption isotherm models such as Langmuir, Freundlich and Redlich–Peterson were evaluated and their constants were derived. The pseudo first order and second order models were employed; the pseudo second order showed a good agreement when compared to pseudo first order.

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## 1. Introduction

Activated carbons (porous carbons) are utilized as adsorbents in a variety of industrial fields for solvent recovery, gas separation, catalysis, etc. [1]. Their properties related to the adsorptive capacity are attributed to their large internal surface area and porosity as well as a marked surface activity [2]. In other words, the pore structure and the chemical nature of the surfaces are important factors in determining adsorptive characteristics of activated carbons. Porous carbon materials play a significant role in adsorption technologies, especially in new applications such as catalytic supports, battery electrodes, capacitors, gas storage, and biomedical engineering [3]. Such applications require the carbon materials to exhibit not only microporous characteristic but it also expected to contain mesoporosity/macropores, because many macromolecules and ions exceed size of micropores [4]. The preparation of various inorganic materials especially activated carbon has been in the focus of materials science since decades.

Activated carbon is prepared by physical activation, i.e., gasification of chars in an oxidizing atmosphere, or by chemical activation, i.e., carbonization of carbonaceous materials impregnated with chemical reagents [5]. The commonly used precursors are bituminous coal, wood, coconut shell, peat, petroleum, pitch, and polymers [6]. Activated carbons produced from various types of carbonaceous materials

have been employed as adsorbents in the above mentioned processes. At the present time, chemical activation is preferred over physical activation for its lowered activation temperature and increased yield. Among the numerous chemical activants such as KOH, ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, HCl, etc., H<sub>3</sub>PO<sub>4</sub> is widely used for this process as it can be removed easily after activation of the carbon by washing with hot and cold water. In the present investigation, the raw material used was rice husk. Rice husk contains organic matter such as sugars, lignin cellulose, protein, etc., and inorganic matter consisting of silica [7]. The manufacture of activated carbon involves two steps. The first step consists of the synchronous process of carbonization of the raw materials in an inert atmosphere, and the second step involves the synchronous process of activation of the carbonized products. The carbonization consists of thermal decomposition of the rice husk materials, eliminating non-carbon species other than silica and producing a fixed carbon mass with a rudimentary pore structure. Very fine and closed pores are created during this step. The purpose of activation is to enlarge the diameter of the pores and to create new pores.

The objective of this study was to produce a low-cost activated carbon with microporous and mesoporous ranges using rice husk as the raw material. Several studies [8–16] on chemical activation using ZnCl<sub>2</sub> have been reported to maximize the adsorptive capacity and bulk density of activated carbons produced from lignocellulosic materials such as peach stones [17–19]. However, phosphoric acid is preferred because it does not entail the problems with corrosion,

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inefficient chemical recovery, and other environmental disadvantages that are associated with  $ZnCl_2$  [20]. Phosphoric acid activation process has been attempted to coconut shell [21]; peach stones [22]; coals and hard woods [23]; and shells of nuts such as almonds, pecans, and English walnuts. These precursors are of cellulosic or lignocellulosic origin. There has been very little study focusing on the use of  $H_3PO_4$  as a chemical activating agent for rice husk.

Amino acids are simple molecules that are the building blocks of proteins and possessing both carboxyl and amino groups whose adsorption behavior could be adequately used toward the understanding of the adsorption of enzymes on solid adsorbents. They are used as supplements to improve the quality of proteins in food technology [24]. On the other hand, the controlled adsorption of amino acid is crucial in the field of biotechnology, where well-ordered amino acid layers may lead to new generation of reactor beds for catalysis and disease diagnostics [25]. Moreover, the adsorption of simple amino acids is the first step of the mechanism of peptide bond formation and chain elongation on solid oxides. From these view points, the adsorption behavior of amino acids on the surfaces of materials such as hydroxyapatite, zirconium phosphate modified silica, silica-gels, activated carbon, zeolite and zeotype materials has been investigated [26]. Glycine, because it is the simplest amino acid, is often regarded as a model compound for the study of these systems. The aim of this work was to investigate adsorption behaviour of glycine from water/methanol solutions on samples onto  $MAC_{800}$ .

## 2. Materials and methods

### 2.1. Materials

Glycine, methanol, Hydrindantin and Ninhydrin, were purchased from Merck (Germany) and used as received. Rice husk (RH) as the precursor material obtained from an agricultural industry was well washed with  $H_2O$  several times for the removal of dust and used after oven drying at  $110\text{ }^\circ\text{C}$  for 6 h. The dried samples were then sieved to about  $600\text{-}\mu\text{m}$  in size, and this fraction was used for the preparation of activated carbon.

### 2.2. Preparation of activated carbon

The activated carbon samples from rice husk were prepared in two sequential steps: pre-carbonization at  $400\text{ }^\circ\text{C}$  and chemical activation. The washed rice husk was packed in an air-tight graphite crucible and heated at  $400\text{ }^\circ\text{C}$  for 4 h. The pre-carbonized material was activated, using ortho phosphoric acid ( $H_3PO_4$ ) in the ratio of 1: 2.3 (carbon:  $H_3PO_4$ ), and sealed in an air-tight crucible. This was followed by heating to one of the three different temperatures 700, 800, and  $900\text{ }^\circ\text{C}$  at a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$  using a temperature programmer and maintained at the final temperature for 1 h before cooling. Finally, the activated carbon was washed with hot water to remove the excess phosphorus compounds until the wash water attained pH 7. The washed activated carbon samples were dried at  $110\text{ }^\circ\text{C}$  to obtain the final product. The samples were heated at activation temperatures of 700, 800, and  $900\text{ }^\circ\text{C}$  to get microporous/mesoporous composites and were labeled as  $MAC_{700}$ ,  $MAC_{800}$ , and  $MAC_{900}$  respectively.

### 2.3. Characterization of the catalyst

#### 2.3.1. Surface area, pore volume and pore size distribution

The surface area and pore size distribution were derived from the  $N_2$  adsorption–desorption isotherms. The  $N_2$  adsorption–desorption isotherms of activated carbon were measured using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). Prior to measurement, carbon samples were degassed at  $150\text{ }^\circ\text{C}$  for overnight. The nitrogen adsorption–desorption data were recorded at liquid nitrogen temperature  $77\text{ K}$ . The surface area of

the activated carbons was calculated using BET equation, which is the most widely used model for determining the specific surface area ( $\text{m}^2/\text{g}$ ). The pore size distribution was determined using BJH method. In addition, the t-plot method was applied to calculate the micropore volume and external surface area (mesoporous surface area).

#### 2.3.2. Elemental (C H N) analysis

The C, H, N content of the different heat-treated carbons were determined using CHNS 1108 model Carlo–Erba analyzer.

#### 2.3.3. X-ray diffraction technique

X-ray diffraction experiments were performed using Philips X'pert diffractometer for  $2\theta$  values from  $10$  to  $80^\circ$  along with low angle, using  $\text{Cu K}\alpha$  radiation at a wavelength of  $\lambda = 1.54\text{ \AA}$ . The other experimental conditions included were  $1/2^\circ$  divergence slits and a 5-s residence time at each step, and the intensity was measured in counts.

#### 2.3.4. X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) was carried out in a VG Scientific ESCALAB-MkII XPS system using  $\text{Al K}\alpha$  radiation.

#### 2.3.5. FT-IR studies

A Perkin-Elmer infrared spectrometer was used for the investigation of the surface functional groups. The carbon samples were mixed with KBr of spectroscopic grade and made into pellets at a pressure of about 1 MPa. The pellets were about 10 mm in diameter and 1 mm in thickness. The samples were scanned in the spectral range of  $4000\text{--}400\text{ cm}^{-1}$ .

#### 2.3.6. $^{29}\text{Si}$ -NMR spectrum of $MAC_{800}$

$^{29}\text{Si}$ -solid state nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker-DSX 300 spectrometer (Germany) at  $B_0 = 7.04\text{ T}$  under the condition of magic angle spinning (MAS) operating at a Larmor frequency  $59.624\text{ MHz}$  at room temperature. The sample spinning speed to external field was  $10\text{ KHz}$ . A  $5\text{ }\mu\text{s}$  width, 15 s pulse delay and a pulse of angle  $60^\circ$  were used. Chemical shifts values are given in ppm relative to internal tetramethyl silane (TMS).

#### 2.3.7. Thermogravimetric analysis

The thermogravimetric analysis (TGA) was employed to study the thermal behavior of the carbon samples in the presence of nitrogen using universal NETZSCH STA 409 C/CD instruments in the temperature range  $20\text{--}1400\text{ }^\circ\text{C}$ .

#### 2.3.8. Scanning electron microscopy

The surface morphology of  $MAC_{800}$  samples before and after the reaction was determined using Scanning Electron Microscope (JEOL, JSM 840 A). The carbon samples were coated with gold by a gold sputtering device (JEOL, JFC-1600) for the clear visibility of the surface morphology.

### 2.4. Batch adsorption of glycine onto $MAC_{800}$

The adsorption of glycine from water/methanol solutions was studied by a batch method using  $MAC_{800}$ . An appropriate quantity of glycine was dissolved in 2 ml of water and required pH was adjusted by adding HCl or NaOH and made up to 1 l using methanol as the solvent. Adsorption kinetics and equilibrium studies were conducted using batch mode adsorption technique by placing a known quantity of the adsorbent in glass bottles containing 20 ml of the above solution of predetermined concentration. The adsorbent dose was  $1\text{ g}/20\text{ ml}$  solution. The solutions were agitated at 100 rpm until the equilibrium was reached at a given particular temperature, pH and concentration as agitation beyond 100 rpm had very little effect on

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