



Effect of Phosphoric Acid Modification on Characteristics of Rice Husk Activated Carbon

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Activated carbon was produced from rice husk via thermal pretreatment preceding chemical modification with phosphoric acid. In order to study the effect of phosphoric acid modification, the characteristics of the activated carbon produced were determined before and after acid modification and subsequently compared. These characteristics include surface morphology, surface functional groups, surface area, average pore diameter and pore volume. Characterization results showed that modification of the thermally treated rice husk with phosphoric acid enhanced the surface area of the activated carbon from 12.47 to 102.4m²/g. The average pore diameter was also enhanced from 2.4 to 1.82nm. It also shows improvement in micropore volume from 0.0052 to 0.034cm³/g. SEM analysis confirmed the improvement in surface area and pore development resulting from the phosphoric acid modification while FTIR analysis revealed the existence of phosphorous-oxy-containing functional groups on the surface of the phosphoric acid modified activated carbon.

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INTRODUCTION

Rice is the third most important cereal crop grown around the world with an annual production of more than 650 million tons [1]. Nigeria is a net importer of rice with an annual local production of 3-4 million tons of paddy rice [2] and about 20-25% of this is rice husk depending on the variety. Rice husk which is a layer protecting rice grain [3] is the major by-product obtained from rice processing mill [4]. It consists of cellulose (32.24%), hemicelluloses (21.34%), lignin (21.44%), water (8.11%), extractives (1.82%) and mineral ash (15.05%) as well as high percentage of silica in its mineral ash, which is 94.5-96.34% [5, 6]. It is abundantly and locally available at almost no-cost but underutilized thereby constituting solid waste in the environment [5]. It is very difficult to decompose and traditionally, it is being disposed on land resulting in esthetic pollution, eutrophication and perturbation in

aquatic life [7, 8]. Over the past several years, attempts have been made in many parts of the world to utilize large quantities of rice husks from rice mills in a beneficial way. These include animal feed, bedding materials, soil conditioner, fertilizer, solid fuel for steam generation, bio-fuel, a source of organic and inorganic chemicals, carbon, catalyst, abrasives components, refractory and insulating materials, paper and board manufacturing, among others [9-11]. Activated carbon can be produced from biomass plant or waste but production from biomass waste is being favored because the former competes for land and water with food crops that are already in high demand which may lead to rise in food prices [12]. In addition, biomass wastes especially agricultural wastes are renewable, very cheap and readily available and utilization of these wastes for the production of activated carbons constitutes a viable option for material recovery and solid waste management [13]. Hence, attention is increasingly focused on the production of activated carbons from agricultural wastes [14].

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As a result, there is ongoing research into modification of these agricultural wastes with the aim of improving their efficiencies and effectiveness in adsorption process. Rice husk is an agricultural waste material that is cheaply available as a by-product of rice processing but requires pretreatment (modification) for better performance as an adsorbent. The pretreatment techniques may be grouped as thermal or chemical process. Girgis *et al.*, [15] reported that in chemical activation, there is preference to phosphoric acid over zinc chloride nowadays which is due to its relative advantage that includes ease of recovery and possible production of activated carbon with porosity of interest by changing the condition of activation. Therefore, the objective of this paper is to highlight the effect of phosphoric acid modification on the characteristics of rice husk activated carbon.

MATERIALS AND METHOD

Production of activated carbon

The natural precursor used in the preparation of adsorbent is rice husk which was collected from National Cereal Research Institute, Badeggi. When collected from NCRI Rice Mill, rice husk was washed with distilled water to remove dirt and surface impurity, then oven-dried at 100°C for 24h [16]. In the thermal pretreatment, rice husk was placed on a ceramic flat surface, charged into a furnace and heated to a temperature of 441.46°C at a heating rate of 20-25°C/min and residence time of 1h. The charred residue was collected and cooled at room temperature. In the chemical pretreatment, the carbonized rice husk (charred residue) was activated with 1M H₃PO₄ for 3h at impregnation ratio of 2:1 (volume *ml* of acid/mass *g* of rice husk) and later oven-dried overnight at 200°C to ensure proper drying [17, 18]. The material was then removed from the oven, cooled for 2h and then washed with distilled water to bring the pH to 7.0 and again oven-dried overnight at 100°C [17].

Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was employed to study the thermal behavior of samples using a thermal analyzer (TGA 4000 Perkin-Elmer). The thermobalance automatically measures the weight loss of the sample as a function of temperature and time. The samples were subjected to pyrolysis under N₂ flow (35 ml/min) with heating rate of 20°C/min [19-22].

Scanning electron microscopy (SEM) analysis

The surface morphology was obtained using Scanning Electron Microscope (Phenom ProX) working at a high voltage of 15 kV. The samples were coated with gold by a gold sputtering device for clear visibility and

conductivity. Thereafter, the coated sample was placed on the sample holder for analysis [23, 24].

Fourier transform infrared (FTIR) spectroscopy analysis

The surface functional groups of the samples were estimated by Fourier Transform Infrared (FTIR) spectroscopy analysis using a spectrometer (Shimadzu 8400s). The pellet for infrared studies was prepared by mixing a given sample with KBr crystals and pressed into a pellet. The pellet which is homogeneous in appearance was inserted into the IR sample holder for the analysis. FTIR spectra of different samples were recorded within 400-4000cm⁻¹ at a resolution of 2cm⁻¹ [25-27].

Surface area and pore size analysis

The surface area and average pore size of samples were determined using a gas sorption analyzer (NOVA 4200e Quantachrome and the Quantachrome NovaWin software). The samples were degassed under vacuum at 200°C for 3h prior to measurement. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature of 77.35K. The adsorption equilibrium time was set at 60s. The Brunauer, Emmett and Teller (BET) method was used to calculate the surface area, using the data obtained from the N₂ adsorption isotherm within the P/P₀ range of 0.05-0.3, where P is the system pressure and P₀ is the initial pressure at 1 bar. The micropore volume (V_{mic}) and the average pore diameter (d_p) were derived from the Dubinin-Radushkevich (DR) method [28-32].

RESULTS AND DISCUSSION

Thermo-gravimetric analysis (TGA)

The TGA profile shows three-step weight loss. The first was observed at less than 150°C (initial 6minutes of residence time) amounting to 5% of the weight loss. This largely account for the removal of water molecules present in the sample. The sample was observed to be virtually stable at temperature range of 150-300°C (Figure 1) corresponding to residence time of 5-14minutes (Figure 2) and representing about 5% weight loss. Thereafter, significant weight loss was observed between 300-415°C (Figure 1) occurring between 14-20min of residence time (Figure 2) and this represent about 50% of the weight loss. This is usually due to hemicelluloses and cellulose decomposition. From 415°C (Figure 1) percentage weight loss was observed to be relatively small which is due to the decomposition of lignin component that degrades slowly over a wide range of temperature [23], hence yield was observed to be almost stable. Figure 2 shows that at 40min of residence time, temperature of 441.46°C resulted higher yield of 34.9% compared to 30.6% obtained from

temperature of 800°C. It was also observed that increasing the residence time from 40 to 80min while maintaining the temperature at 441.46°C did not significantly decrease the yield as it only amounted to 34.01% yield.

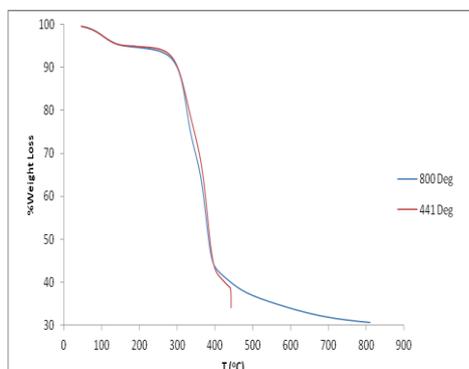


Figure 1. TGA profile for % weight loss against temperature

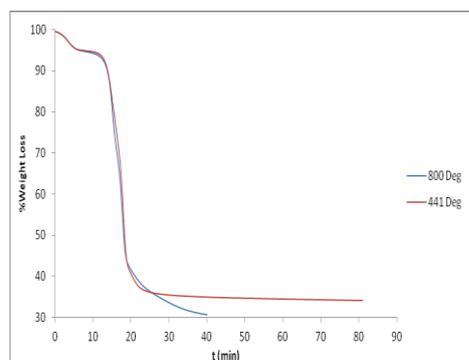


Figure 2. TGA profile for % weight loss against time

Fourier transformed infrared spectroscopy (FTIR)

The FTIR spectrum of the charred residue obtained from thermal pretreatment is as presented in Figure 3 while that of the phosphoric acid modification of the charred residue is as presented in Figure 4. Girgis *et al.*, [15]; Liou *et al.*, [33]; Shi *et al.*, [34] and Nahil *et al.*, [35] reported that for the FTIR spectrum of carbon prepared by phosphoric acid activation, the band in the region of 1300-900 cm^{-1} could be caused by phosphorous-oxy-containing functional groups. Therefore, in comparison the shift in broad band to 1095.6 cm^{-1} observed in Figure 4 could be attributed to P=O in organic phosphates, O-C bond in P-O-C linkage or P=OOH bond. This indicates the presence of phosphorous-oxy-containing group in the activated carbon implying that traces of phosphates remain in the carbon even after repeated washing. The appearance of the broad band in the region 720-590 cm^{-1} in Figure 4 which could be assigned to O-H (out of plane bend) could indicate the introduction of oxy-containing functional groups resulting from phosphoric acid

modification. These oxy-containing functional groups enhance phenol adsorption via interaction such as hydrogen binding and complexation [25].

Scanning electron microscopy (SEM)

The micrographs in Figures 5 and 6 reveal the morphology of the charred residue obtained from thermal pretreatment and the phosphoric acid modified charred residue respectively. Figure 5 shows that the charred residue obtained from thermal pretreatment is characterized by heterogeneous surface. In comparison, phosphoric acid modification of the charred residue as observed in Figure 6 shows that the surface heterogeneity of the activated carbon was significantly reduced. Further comparison of the micrographs reveals that the micrograph in Figure 6 confirmed relative improvement in the surface area and pore development.

Surface area and pore size

Surface area

The surface area of the activated carbon was determined using Langmuir and BET model. Table 1 shows that the charred residue obtained from thermal pretreatment revealed Langmuir (S_L), BET single point (S_{BET1}) and BET multipoint (S_{BET2}) surface area of 12.47, 9.553 and 9.071 m^2/g respectively. It was also observed that the phosphoric acid modification of the charred residue increased the surface area of the rice husk activated carbon to 102.4, 64.7 and 66.13 m^2/g for Langmuir, BET (single point) and BET (multipoint), respectively. This increase in surface area could be attributed to the phosphoric acid impregnation and washing which lead to the removal of unorganized carbon or residual tars materials at low temperatures thereby opening the closed pores [23, 24] or the removal of soluble phosphates formed from the reaction of phosphoric acid and silica deposited into pores [33, 36, 37].

Pore size

The micropore volume was determined using the DR method. Table 1 also shows that the charred residue has micropore volume (V_{mic}) of 0.0052 cm^3/g while phosphoric acid modification enhanced the micropore volume to 0.034 cm^3/g . Therefore, the microporosity of the rice husk activated carbon was increased in volume from 0.0052 to 0.034 cm^3/g as a result of the phosphoric acid modification of the charred residue. It was also observed that prior to the phosphoric acid modification, the charred residue has an average pore diameter (D_p) of 2.4nm. Thereafter, development of micropores was improved via acid modification resulting in average pore diameter of 1.82nm. This could be as a result of the introduction of functional groups on the surface of the smaller mesopores thereby shrinking them to micropores.

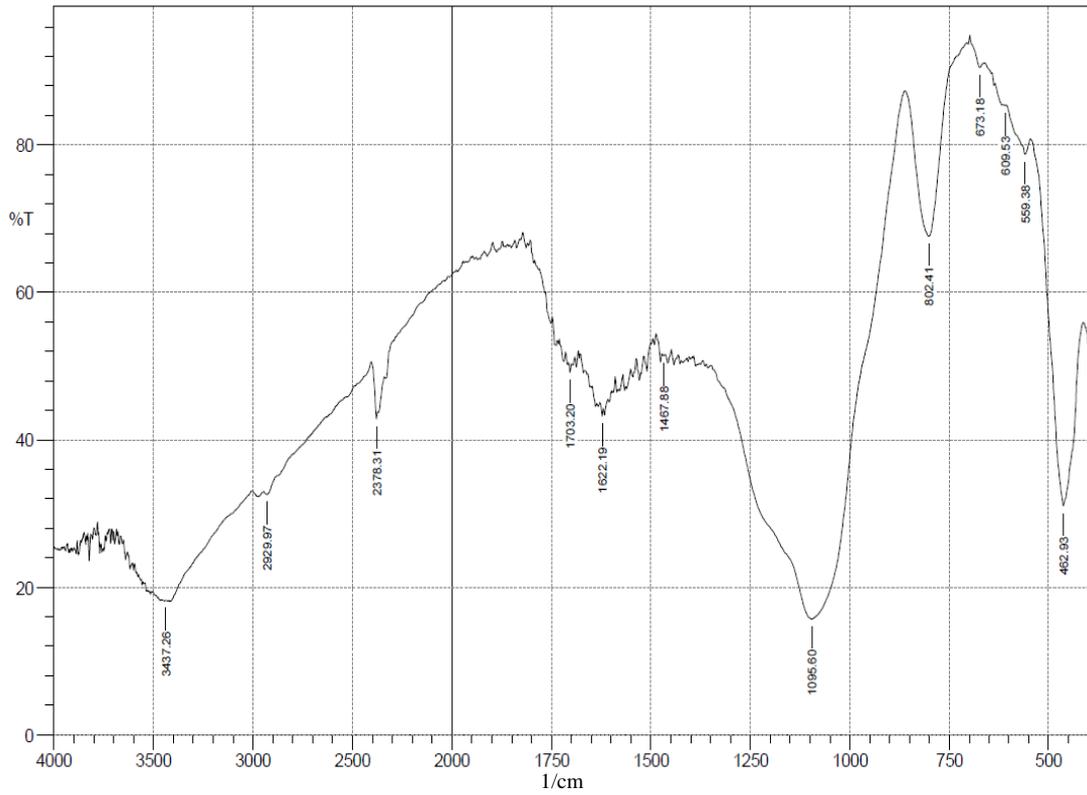


Figure 3. FTIR spectrum before acid modification

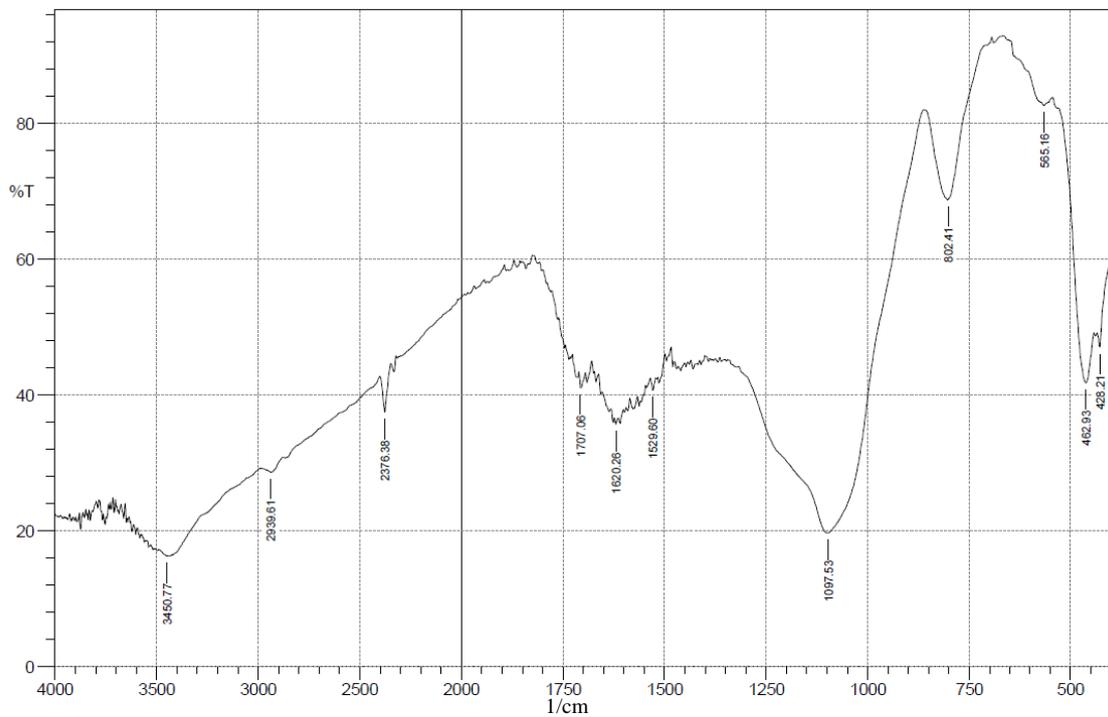


Figure 4. FTIR spectrum after acid modification

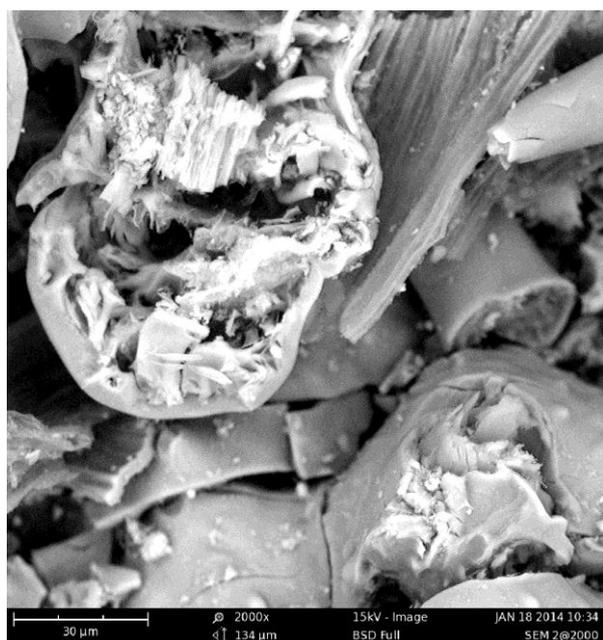


Figure 5. SEM Micrograph before acid modification



Figure 6. SEM Micrograph after acid modification

TABLE 1. Surface Area and Pore Size before and after Phosphoric Acid Modification

Sample	S_L (m^2/g)	S_{BET1} (m^2/g)	S_{BET2} (m^2/g)	V_{mic} (cm^3/g)	D_p (nm)
Before acid modification	12.47	9.553	9.071	0.0052	2.48
After acid modification	102.4	64.7	66.13	0.034	1.82

CONCLUSION

In conclusion, the BET analysis shows that modification of the charred residue with phosphoric acid enhanced the surface area of the activated carbon from 12.47 to 102.4 m^2/g . The average pore diameter was also enhanced from 2.4 to 1.82 nm. It also shows improvement in micropore volume from 0.0052 to 0.034 cm^3/g . SEM analysis confirmed the improvement in surface area and pore development resulting from the phosphoric acid modification while FTIR analysis revealed the existence of phosphorous-oxy-containing functional groups on the surface of the phosphoric acid modified activated carbon. Therefore, modification of thermally pretreated rice husk with phosphoric acid has been noted to result in significant changes in the characteristics of the activated carbon which in turn governs its performance in various areas of application such as wastewater treatment.

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Persian Abstract

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چکیده

کربن فعال با استفاده پیش تیمار دمایی همراه با اصلاح سازی شیمیایی با فسفریک اسید از سیوس برنج بدست آمد. به منظور بررسی تاثیر اصلاح سازی شیمیایی، خواص کربن فعال قبل و بعد از اصلاح سازی تعیین شد. بررسی خواص کربن فعال شامل بررسی مرفولوژی، گروه های عملکردی سطحی، مساحت سطح، قطر میانگین تخلخل و حجم تخلخل می باشد. نتیجه بررسی خواص نشان داد که اصلاح سازی شیمیایی سیوس پیش تیمار شده دمایی با فسفریک اسید سبب افزایش مساحت سطحی کربن فعال از $12/47 \text{ m}^2/\text{g}$ به $102/4 \text{ m}^2/\text{g}$ شد. هم چنین این کار سبب افزایش میانگین حجم سوراخ ها از $1/82 \text{ nm}$ به $2/4 \text{ nm}$ شد. علاوه بر این اصلاح سازی شیمیایی سبب افزایش حجم های میکروسکوپی تخلخل ها از $0/052 \text{ cm}^3/\text{g}$ به $0/034 \text{ cm}^3/\text{g}$ شد. آنالیز SEM افزایش ریزتخلخل ها را پس از اصلاح سازی شیمیایی با فسفریک اسید را تایید کرد درحالیکه آنالیز FTIR وجود گروه های عملکردی فسفری-اکسی بر روی سطح کربن فعال پس از اصلاح سازی شیمیایی را نشان داد.