

## **CRYSTAL AND AMORPHOUS SILICA FROM $\text{KMnO}_4$ TREATED AND UNTREATED RICE HUSK**

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### **Abstract**

*In present research attempt has been made to determine effect of dilute solution of potassium permanganate on rice husk and the quality of amorphous silica obtained by controlled burning of treated rice husk. The rice husk was allowed to react with the dilute solution of  $\text{KMnO}_4$  (0.001N) at room temperature for half an hour. The treated and untreated rice husks were then analyzed by Scanning Electron Microscope (SEM) and by Thermogravimetric Analyses (TGA). The SEM results revealed that the cellulose and organic matters in the protuberances of the rice husk were partially dissolved into the solution of potassium permanganate. TGA of rice husks showed that the thermal degradation of potassium permanganate treated rice husk was relatively faster than the untreated rice husk due to the availability of oxygen from decomposition of  $\text{KMnO}_4$  and due to the reduced cellulose and organic contents. For X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectrometry (FTIR) analyses the pretreated rice husk was heated in tube furnace at  $750^\circ\text{C}$  for one hour. FTIR results revealed that the O-Si-O bond in rice husk ash become weak due to the presence of potassium permanganate. Favorable results were obtained from XRD patterns indicating that potassium permanganate treated rice husk produced amorphous silica of good quality.*

**Key Words:** *Rice husk, Potassium permanganate, Cellulose, SEM, TGA, FTIR, XRD*

### **Introduction**

Industrial importance of rice husk (RH) is due to the presence of silica in hydrated amorphous form. The rice husk contains 80 *per cent* organic volatile materials and remaining 20 *per cent* silica (James and Subbarao 1996). The chemical composition of the rice husk ash varies from RH to RH which may be due to geographical and climatic conditions, type of rice, and the quantity of fertilizer used (Govindarao 1980).

The high silica content in the rice husk is responsible for the residual carbon. It has been reported that rice husk produces more crystal silica when burnt under uncontrolled burning conditions and uncontrolled burning rates, however; amorphous silica of high purity can not be produced just by controlling the burning conditions and burning rates (Krishnarao 2001, Manasaray 1998). The silica in the rice husk is at the molecular level associated with water. It appears in several forms in rice husk such as crystals of quartz and crystallite, tridymite, coesite, stishovite, opal and lechatelrite. Extracting them as amorphous silica from rice husk makes them reactive silica (Natarajan 1998).

Reactive nature of amorphous silica reduces reaction temperature from 1000 °C to 100 °C in sodium silicate formation (Edson and Ederson 2006). (Singh 2006) synthesized  $\beta$ -dicalcium silicate from amorphous silica obtained from rice husk, and also from crystal silica and reported that amorphous silica produces highly reactive  $\beta$ -dicalcium silicate having seven times more compressive strength than  $\beta$ -dicalcium silicates produced from crystal silica. (Jonatas and Marcato 2007) reported the synthesis of  $\beta$ -dicalcium silicate from amorphous silica obtained from rice husk, by solution gel technique and reduced formation temperature from 1250 °C to 800 °C. Two forms of silica dominate in combustion process of rice husk, which are lechaterite, and cristobalite. In order to prepare amorphous silica of good quality, the treatment of rice husk with various chemicals before and after combustion was also attempted previously (Chandrasekhar and Pramada 2005, Bining and Jenkins 1991).

Mineral acid leaching of rice husk is reported to be more effective than untreated rice husk for extraction of amorphous silica. Mineral acids of varying concentrations have been used to remove metallic ingredients and it is reported that the HCl is the most effective than other acids. Researchers also tried organic acids on RHA but it has been found that pretreatment of RH is better than post treatment (Chakraverty and Misra, 1988). Degradation behavior of rice husk treated with various solutions of  $\text{KMnO}_4$  was studied and concluded that low concentration solution favors degradation behavior upon heating (Javed and Naveed 2008).

In the present study an attempt has been made to incorporate potassium permanganate as an oxidizing agent to facilitate the combustion process and to extract amorphous silica of high purity from rice husk. Potassium permanganate upon heating decomposes and liberates oxygen that can help in combustion of the rice husk. The objective of present study is to produce amorphous silica of good quality and quantity and to compare activity of potassium permanganate in rice husk with untreated rice husk.

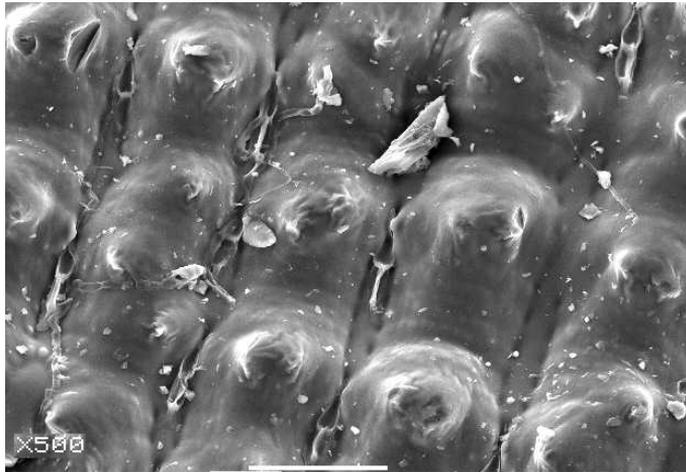
### **Experimental Procedure**

The rice husk was collected from local rice mill during the milling season. The rice husk was first washed with deionized water for five minutes followed by drying in oven at 105°C for 24 hours. A sample of 100 grams was treated with 0.001 N solution of potassium permanganate for 30 minutes followed by drying in oven at 105°C for 24 hours and designated as K1. The untreated rice husk was designated as R. For thermogravimetric analyses the materials K1 and R were ground and passed through twenty mesh sieve by a machine for half an hour.

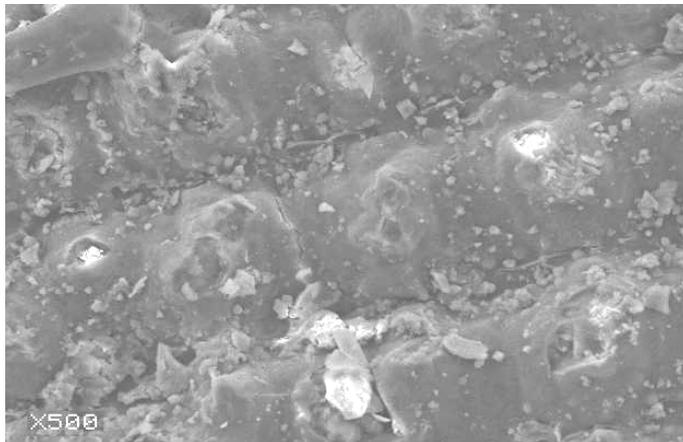
### 1) SEM Analyses

The rice husk samples were fixed on the glass plate with petroleum wax and a thin film of gold was sprayed in a gold-depositing machine. The glass plate was also made conductive by using special conducting liquid. The results of the images are shown in Figure 1.

**Fig.1: SEM of untreated and treated rice husks**  
(a) Untreated rice husk (b) Treated rice husk



**(a)**

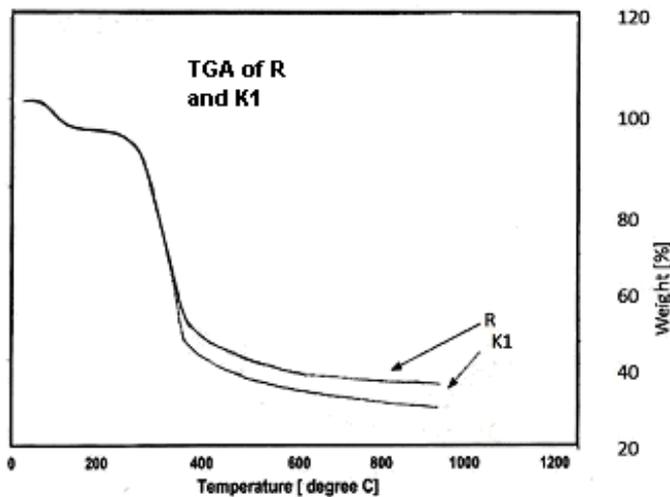


**(b)**

## 2) Thermo Gravimetric Analysis (TGA)

Loss of weight by changing temperature was measured to estimate the rate of thermal degradation. The thermal degradations were performed under nitrogen environment in differential thermal analyzer (TA instruments model Q 600). Nitrogen of ninety nine percent purity was provided by the British Oxygen Company (BOC). The objective of conducting the thermal degradations under nitrogen environment was to analyze the true contribution of  $\text{KMnO}_4$  during thermal degradation. The nitrogen gas was fed at a constant rate of ninety eight ml/minute. The temperature was allowed to rise at the rate of  $10^\circ\text{C}/\text{minute}$  from room temperature to  $1000^\circ\text{C}$ . Approximately 20 mg samples of both (K1 and R) categories were placed in platinum crucible and the loss of weight against increase in temperature was measured. The thermo-grams of TGA are shown by K1 and R in Figure 2.

*Figure 2: Thermogravimetric Analyses of Untreated and Treated rice husks*



## 3) FTIR Analyses

Spectra of FTIR were taken by preparing KBr pellets. Approximately 1 mg of ashes of K1 and R rice husks each was mixed with ninety eight mg of KBr and ground, pressed, and converted into the pellets. The FTIR spectra were scanned in the range of  $400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$ . FTIR spectra were taken on FTIR spectroscopy (JASCO model 4100). FTIR spectra are shown in Figs 3 and 4.

## 4) XRD Analysis

Two porcelain crucibles were selected and filled with R and K1 sieved samples each with 20 grams. Crucibles were then put into the tube furnace (Carbolite) programmed with  $10^\circ\text{C}/\text{min}$  rise from ambient temperature to  $750^\circ\text{C}$ . The tube

furnace then allowed to operate at 750 °C for one hour. Furnace was switched off and allowed to cool down at room temperature. The calcined samples were ground for 30 minutes into fine powders and passed through 300 mesh sieve using automatic vibrating machine.

Samples were dried in oven at 105 °C for 3 hrs before carrying out the XRD analysis using Philips Model PANalytical x-pert pro machine under the following set conditions for each sample:

Scanning Range	Scanning time	X-ray tube Voltage	X-ray tube current Intensity	Step size
5 to 70 degrees	420 seconds	35 KV	35 mA	0.050 degree

The XRD patterns obtained are shown in Figures 5 and 6.

**Results and Discussion.**

TGA analyses can be divided into three zones namely initial, passive and active zones. The weight loss up to 110°C is due to the vaporization of light volatile matters and water which is physically absorbed. Most of the thermal degradation takes place in the active zone that starts from 240°C and terminates at 385°C. In this zone decomposition of primary hemicelluloses and cellulose takes place (Mansaray and Ghaly 1998). Passive zone after active zone starts around 385°C and terminates at around 850°C is due to the decomposition of lignin compounds. The slope of the indices in both zones differ and it may be concluded that the hemicelluloses and cellulose are the main ingredients in thermal degradation process while lignin gets converted itself into char that took much longer time to degrade. It can be seen from Fig. 2 that the degradation of pretreated rice husk K1 is faster than untreated rice husk R in both active and passive zones under similar conditions.

Residual weights obtained from the indices (Fig.2) are shown in Table 1.

*Table 1: Residual weights obtained from TGA indices*

Residual weights %		
T °C	R	K1
400	47	42
500	43	37
600	40	35
700	39	33
800	37	31

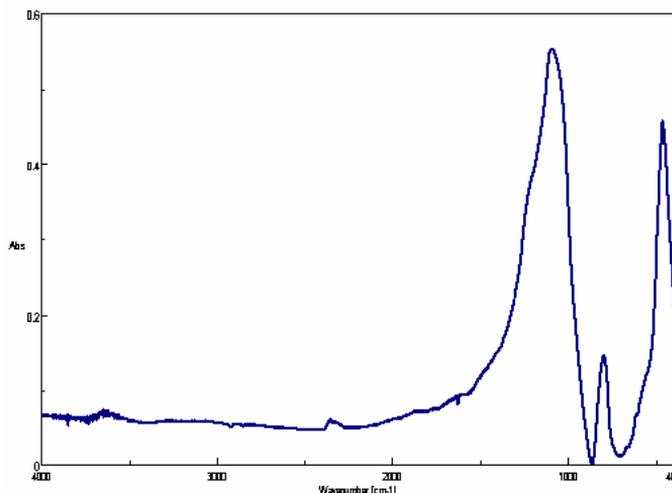
It can be seen that the weight loss of sample K1 from 400°C to 800°C is higher than that of R because of better thermal degradation behavior of sample K1. The

thermal degradation of K1 is faster due to availability of the oxygen from decomposed potassium permanganate. The potassium permanganate upon decomposition at 300 °C liberates oxygen which accelerates thermal degradation process and its effect can be observed in both active and passive zones.

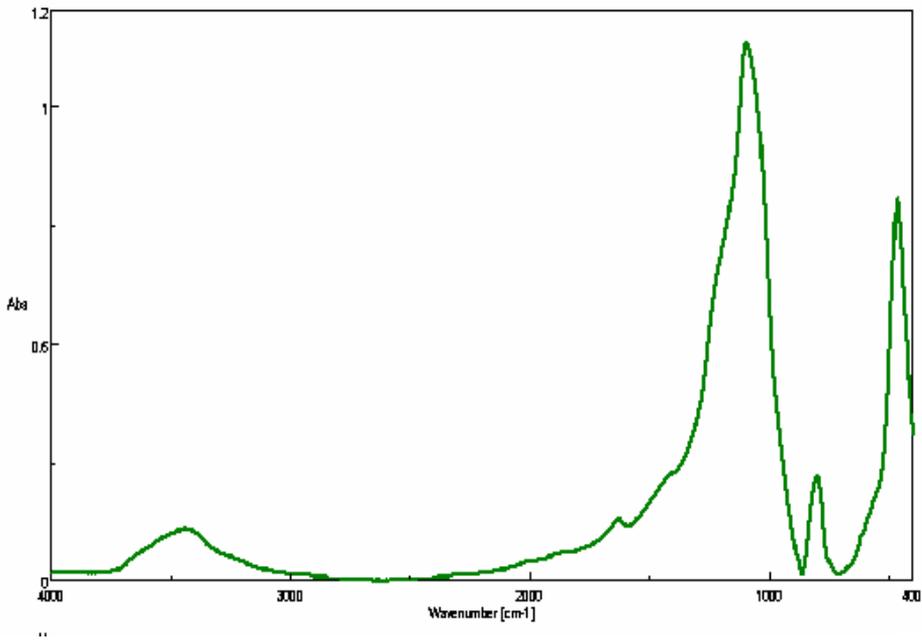
SEM images of both untreated and treated rice husks are different. The ruptured protuberances of pretreated rice husk are due to reaction with  $\text{KMnO}_4$ . It has been reported that  $\text{KMnO}_4$  reacts with cellulose and organic matters at room temperature and forms the complex compounds (Varhegyi and Szabo 2004). The ruptured surface of the rice husk is due to the dissolution of cellulose in  $\text{KMnO}_4$  solution. It may be concluded that the presence of potassium permanganate not only facilitates the thermal degradation of rice husk in active and passive zones but also reduces the cellulose and organic contents in the rice husk. The reduced cellulose and organic contents improve the thermal degradation activity in the active and passive zones.

FTIR spectra show four bands as shown in Figures 3, 4. The bands from  $465\text{ cm}^{-1}$  to  $485\text{ cm}^{-1}$  belongs to bending vibration of O-Si-O. Also the bands from  $1090\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$  and from  $790\text{ cm}^{-1}$  to  $815\text{ cm}^{-1}$  belongs to O-Si-O stretching vibrations. Bands from  $3450\text{ cm}^{-1}$  to  $3640\text{ cm}^{-1}$  are due to the chemically absorbed water and also due to the surface hydroxyl groups. The observed intensity of band K1 at  $3640\text{ cm}^{-1}$  in Figure 6 is highest indicating more chemically absorbed water.

**Fig. 3: FTIR spectra of RHA obtained from untreated rice husk indicating strong O-S-O bond**



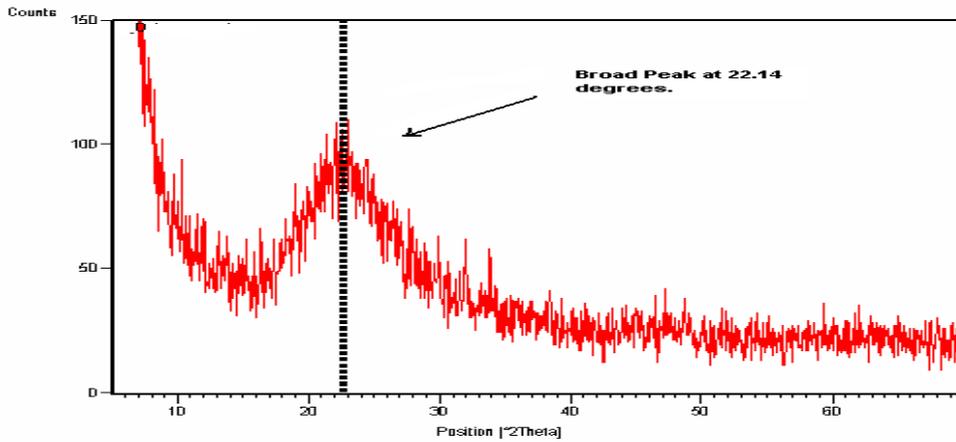
**Fig. 4: FTIR spectra of RHA obtained from treated rice husk indicating weak O-S-O bond**



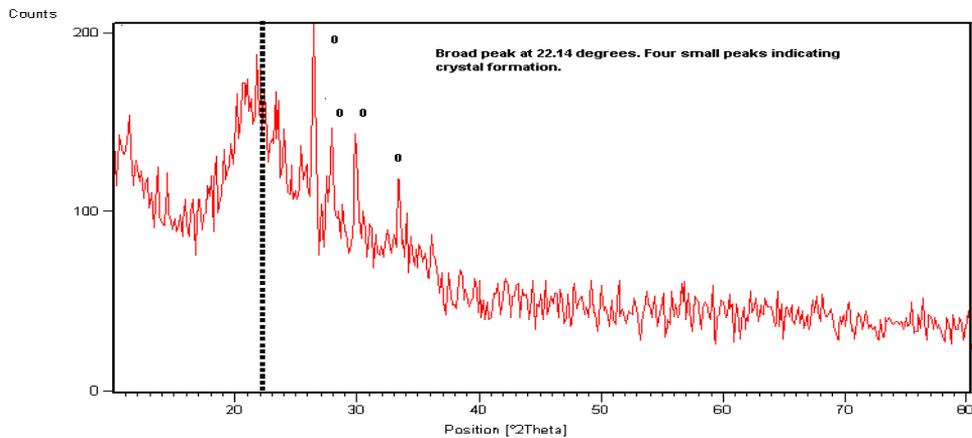
In Figure 4 the bands are of high intensity indicating weak bond strength where as in Figure 3 the intensity of the bands is low indicating high bond strength. The bands of high stretching and bending vibrations are due to the weak bonds in O-Si-O where as low stretching and bending vibrations are due to strong bonds. Low vibration intensity indicates the crystal formation in the ashes at 750 °C. Noticeable crystal formation took place after 750 °C.

The X-Ray diffraction patterns generated by the XRD machine for the ashes are shown in Fig. 5 and 6. It can be seen that all broad diffused peaks at Theta = 22.14 degrees confirming the formation of amorphous silica and very little crystal silica. It has been reported that diffused broad peak at Theta = 22.141 degrees shows the formation of amorphous silica with minute amount of crystal silica (Ikram and Akhtar 1988). The small four peaks for the case of sample R indicate higher quantity of crystalline silica after heat treatment under similar conditions. For the case of sample K1, under same conditions, the broad peak is diffused at Theta = 22.141 degrees without any small or short peak is an indication of amorphous silica. It can be concluded by comparative study of XRD results that  $\text{KMnO}_4$  has helped in oxidation and formation of amorphous silica of high purity.

**Fig. 5: XRD of amorphous silica obtained from sample K1 indicating broad peak diffused at 22.14 degrees, the characteristic of pure amorphous silica.**



**Fig. 6: XRD of crystal silica obtained from sample R has four small peaks indicating more crystal silica than amorphous silica**



## Conclusions

The purpose of treating the rice husk with potassium permanganate is to produce amorphous silica of good quality by thermal treatment. The rice husk was treated with 0.001 N solution of potassium permanganate and then analyzed by Scanning Electron Microscope (SEM) and Thermogravimetric Analyses (TGA). SEM results revealed that the protuberances of the rice husk reacted with  $\text{KMnO}_4$  and reduced the cellulosic and organic contents. Thermogravimetric analyses were performed under nitrogen environment. It has been observed in TGA that pretreated rice husk thermally degraded faster than untreated rice husk in both active and passive zones due to availability of oxygen from decomposed

potassium permanganate and also due to less cellulose and organic contents. The quantity of amorphous silica from K1 is higher than the R in passive zone. Treated and untreated rice husks were heated in tube furnace at 750 °C for one hour to produce amorphous silica and then analyzed by X-Ray Diffraction and FTIR. Patterns obtained from XRD confirm the pure amorphous silica formation in case of pretreated rice husk. Untreated rice husk produced amorphous silica along with crystal silica. The FTIR results revealed that untreated rice husk produces more crystal silica than treated rice husk. It can hence be deduced that  $\text{KMnO}_4$  not only reduces the cellulose and organic contents of the rice husk but also acts as an oxidizing agent during thermal degradation. Reduced cellulose and organic contents and availability of sufficient oxygen both are helpful in thermal degradation of rice husk and produces high purity amorphous silica.

### **Acknowledgements**

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