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Preparation and characterization of activated carbon & amorphous silica from rice husk

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Abstract

Activated carbon (AC) was prepared by the conventional carbonization and KOH activation and amorphous silica was extracted by alkali extraction followed by acid precipitation from rice husk on a laboratory scale. The performance of the produced activated carbon and amorphous silica were examined using I2 value measurement, methylene blue (MB) adsorption test, pH measurement, FTIR and SEM-EDX analysis. The optimum temperature for production of AC was obtained at 700 °C. The AC by alkali extraction method was show higher activity than KOH activation. The maximum I2 value, MB adsorption value & pH value shows at 700 °C followed by alkali extraction with 15% NaOH, which were 510.82 mg/g, 61.1 mg/g and 7.32 respectively. The FTIR analysis shows presence of Si-O-Si bond with a strong peak at 1078.28 cm⁻¹. The SEM image of silica sample shows that the most of organic component is burnt out during combustion.

Keywords: Activated carbon; KOH activation; Carbonization; Amorphous silica; Alkali extraction

Introduction

Rice husk (RH) is an agricultural waste abundantly available in rice-producing countries. They are the natural sheaths that form on rice grains during their growth. These husk have no commercial interest as they are removed during refining of rice (Real *et al.*, 1996). Increase of environmental awareness has led to a growing interest in researching ways of an effective utilization of rice by-product, from which rice husk is particularly valuable due to its high content of amorphous silica (Shigetaka *et al.*, 2005; Yamaguchi *et al.*, 2006). The RH contains 80% organic volatile matters and remaining is silica.

The chemical composition of the RH ash varies from sample to sample which may be due to the different geographical conditions, type of paddy, climatic conditions and type of fertilizer used (Bining and Jenkins, 1992; Houston, 1972). It was found that RH char contains amorphous silica in addition to amorphous carbon as the main constituents (Yamaguchi *et al.*, 2006). Many authors have concluded that rice husk is an excellent source of high grade amorphous silica (Chen and Chang, 1991; Ghosh *et al.*, 1991; Nandi *et al.*, 1991). This portion of the silica cannot be dissolved in alkali and can withstand very high temperatures (Patel *et al.*, 1991).

Production of activated carbon from rice husk has also have peoples interests. Active carbon has good adsorption property, can be produced from a variety of raw materials, such as packing papers, plastic bottles, by-products of the timber industry (e.g. sawdust), straw, rice husk, seeds or fruit shell can be mentioned. Interest is growing on agricultural waste for the production of activated carbon. Production of activated carbon from rice husk is achieved through activation with chemical or physical means (Alvarez *et al.*, 2015; Van and Thi, 2014). Chemical impregnation with KOH, NaOH, ZnCl₂ or H₃PO₄ of pyrolysed rice husk followed by activation at 650–850°C results in activated carbons with extremely high surface areas (750–3014m²/g) (Guo *et al.*, 2002; Kalderis *et al.*, 2008). The chemicals used to remove the silica so as to increase the pore in the rice husk. The RH ash is high in silica content and the loose wet structure of rice husk is destroyed after rice husk combustion in high temperature. While silicon dioxide is extracted from the RH ash, the carbon content is increased greatly in the residue, which is more economical for active carbon preparation in order to realize the farthest value of the agricultural waste.

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The objective of the research was to production of AC and amorphous silica from rice husk and characterize for efficient utilization of waste materials. The properties of amorphous silica and activated carbon from these locally available rice husks from Bangladesh are comparable to some other studies (Liu *et al.*, 2012; Liu *et al.*, 2011).

Materials and methods

Sample Collection

The Rice husk has been collected from Gazipur in Bangladesh. The collected rice husk has 8-10 mm length, 2.0–2.5 mm width and 0.1–0.15 mm of thick. The chemical properties of the collected rice husk sample were determined by proximate and ultimate analyses. Proximate analysis has been done according to the American Society for Testing Materials (ASTM, 1994).

Chemicals

Potassium Hydroxide (Merck KGaA, Germany), Hydrochloric Acid (Caledon, TMG), Sodium Hydroxide (Merck KGaA, Germany), Sodium Thiosulfate (BDH, England), Iodine (Merck KGaA, Germany), Potassium Iodide (Fair Lawn, USA), Potassium Iodate (BDH, England), Starch (Sigma Aldrich, GmbH), Sodium Carbonate (Merck KGaA, Germany), Methylene Blue (LOBA Chemical, India) and Sodium Chloride (Merck KGaA, Germany). All chemicals except solvents were used as received. Solvents were dried by standard methods and distilled under an inert atmosphere.

Preparation of raw materials

The rice husk was washed thoroughly with distilled water to remove adhering soil and clay and then dried in air at 105 °C in an oven for 24 hours. The rice husk was milled and then passed through different sieves. The particle size between 500-250 µm was selected for further pretreatment.

Reactors for pyrolysis

Activated carbon was produced from the above starting materials by carbonization in a horizontal tube furnace. The reactor is made of 1.5 m long steel tube with 100 mm internal diameter. The temperature is controlled by a proportional integral derivative (PID) temperature control and also a thermocouple placed at the center. To maintain the inert atmosphere purified nitrogen gas (99.99%) were used and flow rate was control by using flow meter. Preparation of Activated Carbon (AC) by chemical activation and preparation of Amorphous Silica by alkali (NaOH) extraction method shows in Fig. 1 and Fig. 2 respectively.

Characterization of activated carbon

Iodine value

To gain the knowledge of porous structure of activated carbon, iodine adsorption from liquid phase was adopted by other researchers (Martin *et al.*, 2003) in the characterization of sludge-based activated carbons. The adsorption of aqueous I₂ is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm (Bacaoui *et al.*, 2001). The iodine value was measured according to the procedure established by the American Society for Testing and Materials (ASTM, 1994). The mean values of data for each experiment were presented. Standard deviation was calculated from triplicate samples. Iodine Number is accepted as the most fundamental parameter used to characterize activated carbon performance.

Methylene blue value

The methylene blue value gives an indication of the adsorption capacity of an activated carbon for molecules having similar dimensions to methylene blue. It is a quick method for comparing different batches of activated carbon of the same quality. The amount of standard methylene blue decolorized (in mg) by per gram of carbon (dry basis) is called methylene blue value. The higher number of methylene blue value indicates the higher adsorption capacity of activated carbon.

pH value

Activated carbon carrying inorganic and chemically active group on the surface may alter the pH of liquids to which it is added. A predictive standard test giving a good approximation of actual conditions has been devised. In this case, the carbon sample was extracted with boiling water and the pH of the extract has been defined as the pH value of the activated carbon.

Characterization of amorphous silica

SEM-EDX

The surface morphology of the amorphous silica was analyzed by using a scanning electron microscope (SEM) Philips, Quanta FEG 200 model equipped with an EDX spectrometer from Oxford instruments. XT microscope software was used for data acquisition and analysis. The measurement was performed at high vacuum mode with the accelerating voltage of 20 kV. Magnification range was 400X - 50000X and the resolution was ≥ 0.2 µm.

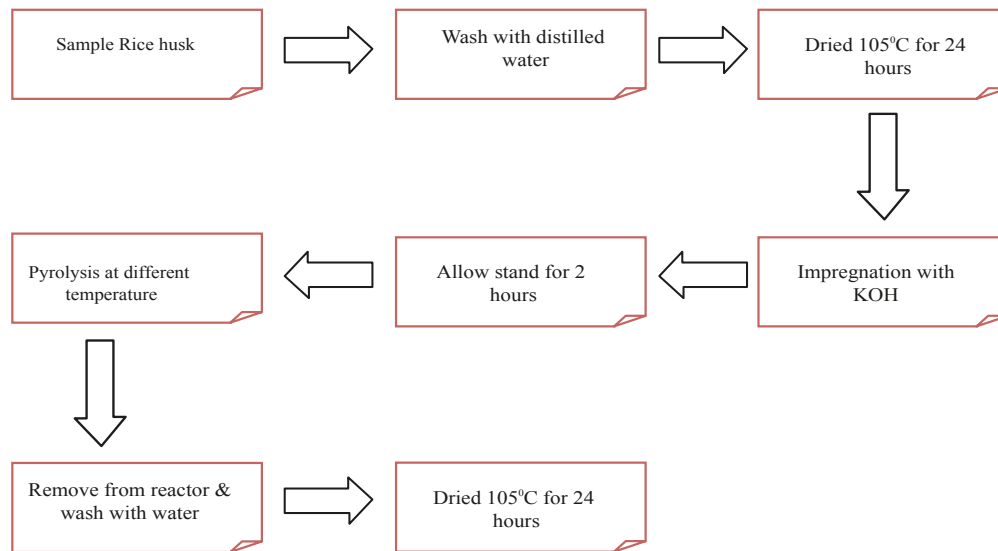


Fig. 1. Flow diagram of preparation of activated carbon by chemical activation

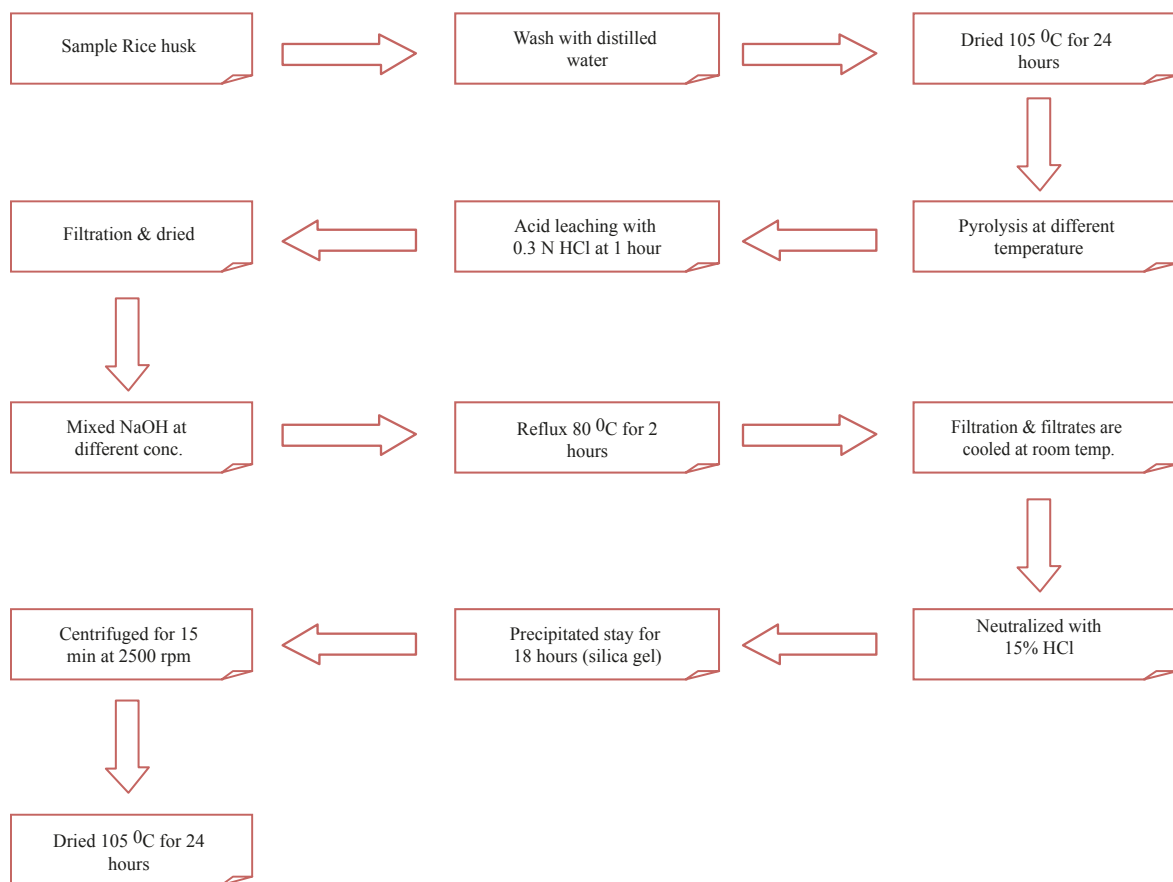


Fig. 2. Flow diagram of preparation of amorphous silica by alkali extraction method

FTIR

FTIR analysis was made using IPrestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan). Sample of 0.1 g was mixed with 1 g of KBr (Merk, Germany) in a mortar. Part of this mix was introduced in a cell connected to a piston of a hydraulic pump giving a compression pressure 15 kPa/cm². The mix was converted to a solid disc which was placed in an oven at 105 °C for 4 hours to prevent any interference with any existing water vapor or carbon dioxide molecules. Then it was transferred to the FTIR analyzer and a corresponding chromatogram was obtained showing the wave lengths of the different functional groups in the sample which were identified by comparing these values with those in the library.

Results and discussion

Raw materials analysis

Table I. Proximate and ultimate analysis results of collected rice husk

Ultimate (wt %, dry and ash free basis)		Proximate (wt% , as received)	
Carbon	37.6	Moisture	11.2
Nitrogen	0.4	Volatile matter	51.9
Hydrogen	4.7	Fixed carbon	14.4
Oxygen	31.5	Ash	22.3
Sulfur	0.0		

Proximate and ultimate analysis results of collected rice husk sample have shown in Table-I. The ash and fixed carbon of the analyzed char is in favor of Activated Carbon and Amorphous Silica production. The content of each of them depends on rice variety, soil chemistry, climatic conditions, and even the geographic localization of the culture. In rice husk the fixed carbon varies from 12 to 18 and ash content varies from 17 to 22 (Iyer *et al.*, 1997)

Effect of KOH activation and silica extraction by alkali on the AC yield

The Activated carbon was produced at different temperature in view to optimize the process. The mass decreased during activation was called activation burn-off and this varied with varying activation temperature. These yields of activated carbon at different temperature are summarized in Fig. 3. The yield of activated carbon decreased with increasing temperature due to the increase of the activation burn-off. The carbon yield of alkali extraction method was strongly depends on the amount of NaOH used. NaOH increase the

dissolution of silica from rice husk into sodium silicate solution as a result the carbon yield has decreased (Fig. 3).

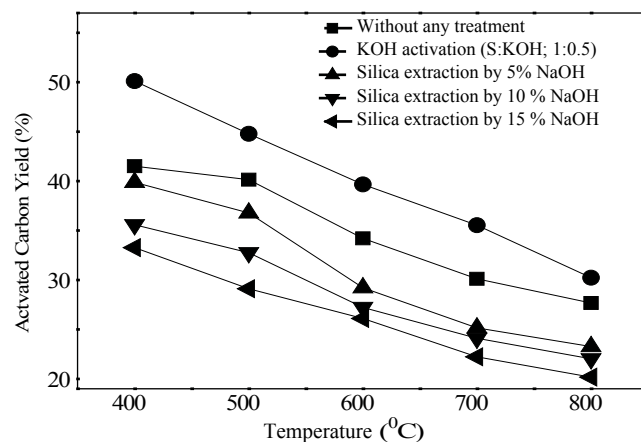


Fig. 3. Activated carbon yield with pyrolysis temperature (for 2 h)

I₂ value and MB adsorption capacity of activated carbon

The activation temperature is a very influential parameter on the pore structure of activated carbon, which determines the adsorption capacity (Hu and Vansant, 1995). The variation in iodine values of AC was investigated as a function of activation temperature. Fig. 4. shows there are no linear relationship between activation temperature and iodine value. This may due to increase micro pores with increasing activation temperatures (Assadullah *et al.*, 2007). The pore size increase up to 700 °C then the pore will become thinner and at a time breakdown occurred and the number of pores was reduced. As a result the surface area and iodine number decreased at high temperatures. Thus calculated the optimum iodine value was at 700 °C. Methylene blue adsorption capacity also increased with increasing of activation temperature until 700 °C (Fig. 5). This may due to increase the surface area up to 700 °C. After that the surface area decreased due to closed of porosity. Another same result has explained by Gyu Hwan Oh and Chong Rae Park, 2002.

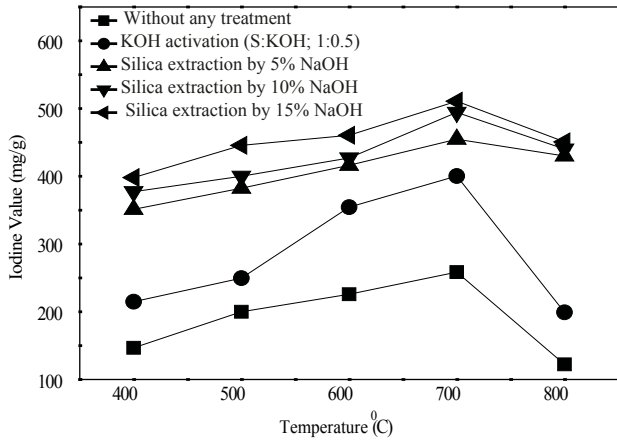


Fig. 4. Iodine value with pyrolysis temperature (for 2 h)

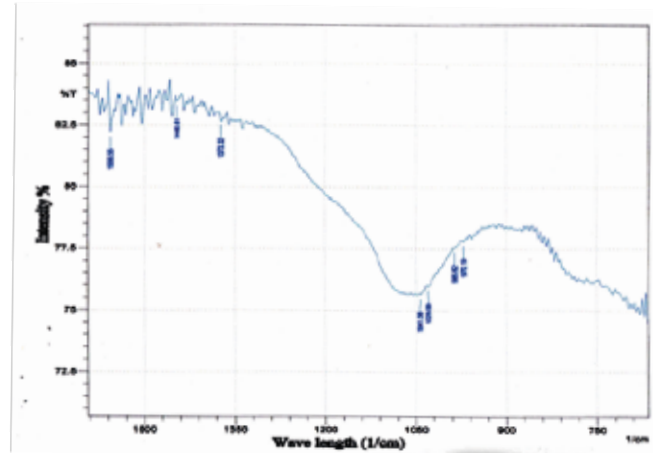


Fig. 7. FTIR spectra of activated carbon

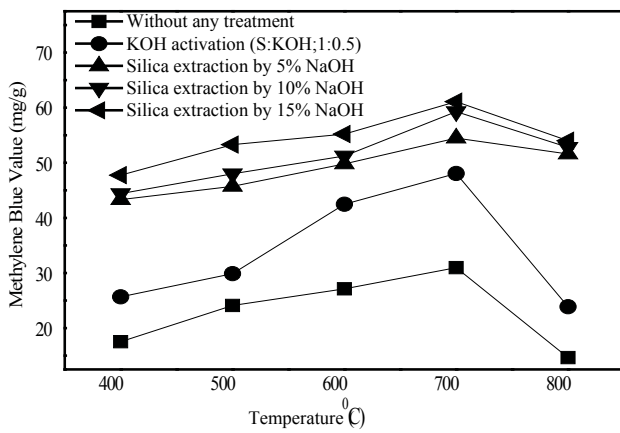


Fig. 5. Methylene blue value with pyrolysis temperature (for 2 h)

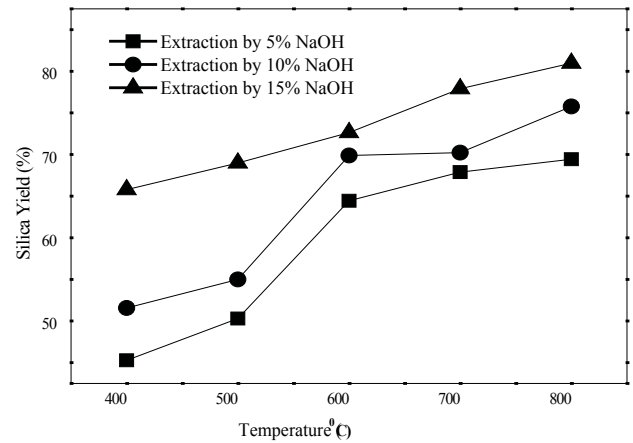


Fig. 8. Effect of NaOH and pyrolysis temperature on silica yield

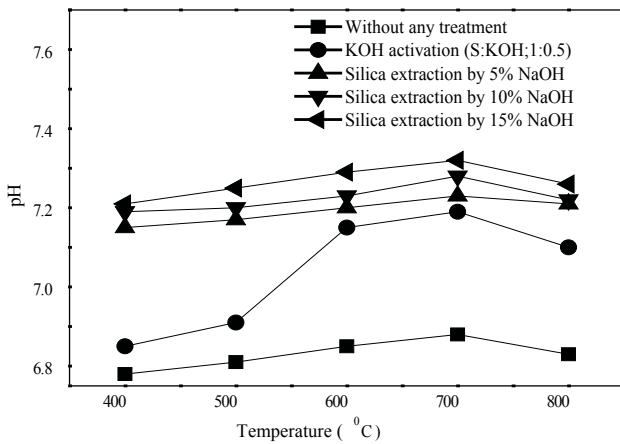


Fig. 6. pH value with pyrolysis temperature (for 2 h)

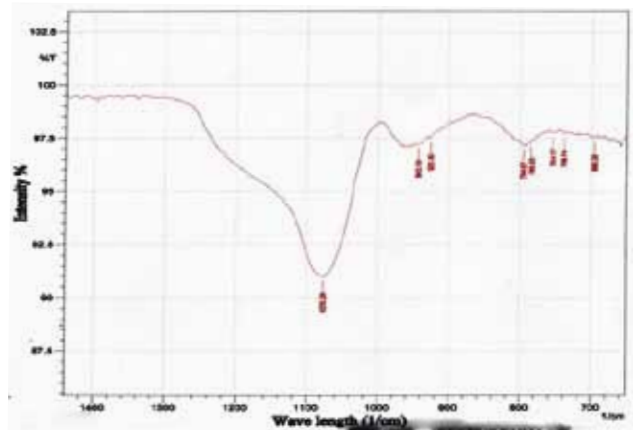


Fig. 9. FTIR spectra of amorphous silica

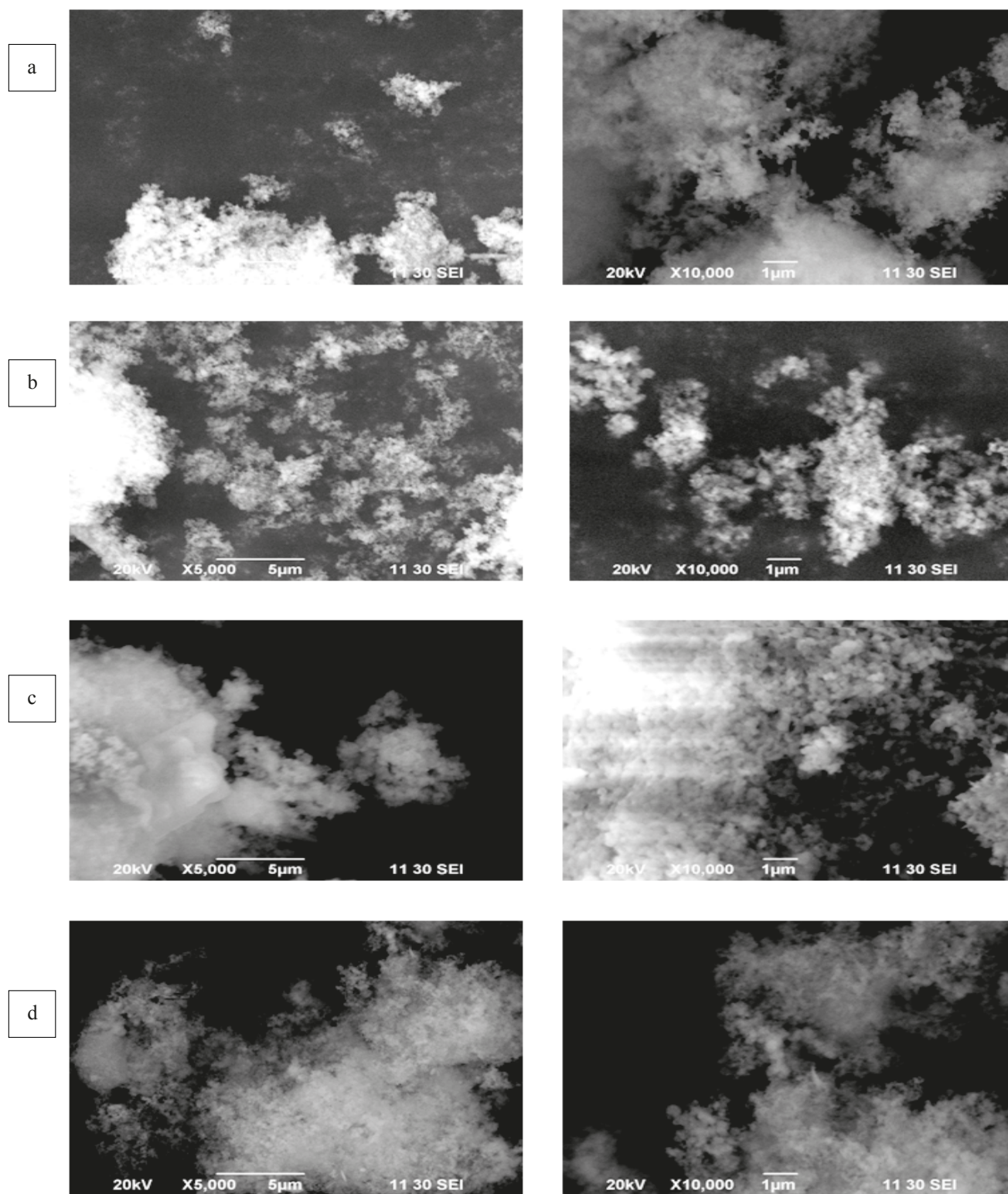


Fig. 10. SEM image of silica at different pyrolysis temperature (a) 400 °C (b) 500 °C (c) 600 °C (d) 700 °C

Considering the dimension of methylene blue molecule is greater than that of iodine. That's why at a specific temperature the iodine value is greater than methylene blue value (Guo Y et al., 2000). Si-O bonds are liberated from the long polymeric chains (Si-O-C/Si-O-Si) at elevated temperatures (Gorthy and Pudukottah 1999). As a result the surface of carbon may be increased due to liberated Si-O bonds. When the pyrolysis temperatures were increased over 700 °C more Si-O was liberated but it may cause the destructive effect to the pores which reduced the surface area. This SiO₂ was removed by alkali extraction with three different concentration of NaOH. That's why the residual carbon had higher surface area than other (Fig. 4 and Fig. 5).

Effect of pH value

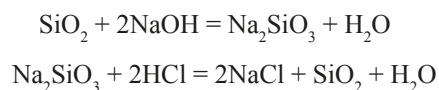
pH of activated carbon can be defined as the pH of a suspension of carbon in distilled water. Activation process increased the surface area and porosity as well as the surface basicity of activated carbon. It is due to presence of oxygen molecule in the surface. That's why larger quantities of methylene blue were adsorbed at higher pH. The adsorption capacity will increase with increasing pH value which also increases up to 700°C (Fig. 6). After that the pH will decrease. The same results also have been seen by Santhi and Manomani, (2009).

Functional Group Analysis of AC

The FTIR spectra were recorded for qualitative characterization of surface functional groups of the activated carbon. Fig. 7. shows that the alkyl aromatic carbon structure (C-H stretching bands at 900-700 cm⁻¹) with numerous oxygen containing functional groups: C-O-(C) (1375 cm⁻¹) and C-O-(H) (1050 cm⁻¹). The band of the spectra (1600 cm⁻¹) can be due to aromatic skeletal mode (Sun and Tomkinson, 2001; Bouwman and Freriks, 1980).

Effect of NaOH and pyrolysis temperature on silica yield

Silica yield increased with the increasing concentration of NaOH and also with the increasing temperature of pyrolysis. Fig. 8. shows the effect of NaOH and pyrolysis temperature on silica yield. Because Si-O parts were liberated from the long polymeric chains (Si-O-C / Si-O-Si) with temperature (Gorthy and Pudukottah 1999). As a result the yield of silica may increase due to liberated Si-O bonds. This SiO₂ is removed by alkali extraction.



Functional Group Analysis of Silica

The major chemical groups present in the silica were identified by FTIR spectra. The IR spectra of silica can be seen

in Fig. 9. It showed very strong bands at the wave number 1076.28 cm⁻¹ due to asymmetric stretching of Si-O-Si group. The IR band for silanol groups were showed at 943.19 cm⁻¹. Si-O stretching for alkali silicate glasses showed at 794.67 cm⁻¹, at 794.67 cm⁻¹ for Si-O-Si symmetric stretching vibrations and band at 460-480 cm⁻¹ is due to O-Si-O bending vibration.

Surface morphology analysis of silica

The morphological features of the amorphous silica observed by scanning electron microscopy (SEM) at different temperature are shown in Fig. 10. From these figures it is clearly seen that amorphous silica has porous and multifaceted particle shape and size. The morphology seen in figure can be attributed to the burning out of the organic component in the rice husk during combustion. The primary particles size showed a tendency to from bigger particles (aggregates). The hydrated silica subsequently polymerizes to form a skeletal silica network which may explain in the SEM micrograph in Fig. 10.

Conclusion

Experiments were conducted to investigate the potential of rice husk as a raw material for the production of activated carbon and amorphous silica. The optimum temperature for production of activated carbon of highest activity was obtained at 700 °C with KOH impregnated rice husk and NaOH extracted char. The result of silica yield (%) increase with increasing temperature and concentration of NaOH for extraction. The SEM image show that amorphous silica has porous and multifaceted particle shape and size & most of organic component is burning out during combustion. Experimental result show that it was feasible to produce activated carbon and amorphous silica from rice husk by the conventional carbonization followed by alkali extraction and by chemical activation method using potassium hydroxide as activating agent.

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