

Synthesis, characterization of Silica Obtained from Rice Husk and Determination its Silica Content by Modified Volumetric Method

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Abstract

The objective of the work was to develop pure silica with high surface area from rice husk by chemical and heat treatment. The silica samples were characterized in terms of chemical composition, particle size distribution, morphology and surface area. The amount of silica was determined by a modified volumetric method. The trace impurities in silica were quantitatively determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES). A 99 % silica powder with surface area 282 m²/gm could be produced by chemical and heat treatment at 1000 °C for 2 h.

Introduction

Rice husk is an agricultural waste material abundantly available in rice producing countries. This husk can be used as an additive for cement and concrete fabrication [1, 2]. Rice husk contains high silicon as a consequence it has become a source for preparation of elementary silicon [3,4], especially silica [5,6], silicon carbide [7], silicon nitride [8] and a number of silicon compounds. Utilization of rice husk as a resource of silica is based on removal of impurities with low effort and the high specific surface. In literature various methods have been reported for the fabrication of silica [9-11].

The application of silica obtained from rice husk is purely depending upon various phenomenons such as the purity of silica, surface area, particle size, porosity etc. Therefore it is very essential to determine the exact quantity of silica. The conventional gravimetric method [12] for estimation of silica, involving insolubilization of silicic acid by dehydration is slow and lengthy. A volumetric method, first described by Travers [13], after that modification of this method was reported by several authors [14-15]. We have slightly modified the described method by Dasgupta et.al. and determined the silica content of the sample. Present study deals with the synthesis, ch-

aracterization of silica obtained from rice husk and determination of silica content by modified volumetric method.

Experimental

Reagents and apparatus

For the synthesis of silica hydrochloric acid (HCl), sodium hydroxide (NaOH), nitric acid used were all of AR/GR grade from E Merck (Germany). Powder of Rice husk was obtained from local rice mill. The standard stock solutions (1000 mg/L) of different metal ions were prepared in 5% nitric acid or hydrochloric acid and subsequent dilution were made in de-ionized water to match sample matrix. Chemical analyses of the impurities in silica were carried out by ICP-AES (Spectroflame modula FTM 08). Infrared Spectrograph were recorded by using Perkin Elmer make, lamda 40 IR instrument while the microstructure were examined by Scanning Electron Microscopic (SEM) technique (SE-440, Leo-Cambridge, Cambridge, UK).

Preparation of Silica

Rice husk obtained from rice mill were washed several times with DI water then dried at 100 °C in air oven for 3 days and finally were grinded to 100-

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mesh size. For the preparation of silica 40 gm of the grounded powder were treated with 30 mL of conc. Sulfuric acid. Charred rice husk was kept at 100 °C on a hot plate for 24 hrs. Carbonized material thus obtained was washed thoroughly with water followed by washing with sodium hydroxide solution to remove free acid. The washed material was further treated with 3N HCl to remove all the trace impurities present in the rice husk. The material was washed thoroughly and dried at 100 °C for 24 hrs. Finally the material was sintered at temperature 600 °C, 800 °C and 1000 °C at a rate of 50 °C /min for 2 h in a furnace to obtain silica sample 1, 2 and 3 respectively.

Result and Discussion

Analysis of metallic impurities in rice husk and silica

Analyses for some common metallic impurities present in the rice husk and silica samples were performed using ICP-AES. For the chemical analyses exactly 0.2 g powder sample were taken in a platinum basin. About 2 mL conc. HClO₄ and 5 mL HF were added slowly to it in sequence and the basin was heated slowly on a hot plate to dryness. This process was repeated three times to remove all silica content of the sample. 10 mL DI water was added to the dry residue and was allowed to evaporate, the process was repeated several times to make it free from excess acid leaving only the metallic constituents. The metallic residue thus left in the basin was dissolved in 5 mL conc. HCL and the volume made up to exactly 25 mL by repeatedly washing the basin

with water. The impurities constituents in the silica samples were determined using ICP-AES after calibration the instrument with reference to standard solution of respective elements.

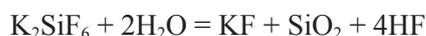
Estimation of silica

In this paper we have modified the reported method [15] to get more accurate results by controlling the temperature of fusion at 550 °C and strictly maintaining the temperature at below 4 °C during washing of K₂SiF₆ precipitate up to neutralization of the excess acid after transferring the precipitate. Further ten pellets of KOH was fused in a nickel crucible in a burner and allowed to cool. 0.02 g of powder sample was transferred in to the Ni crucible containing fused KOH. The crucible was covered with lid and fused in burner by slowly raising temperature to 550 °C. The melt was kept for 15 minutes with occasional swirling. The crucible was cooled and placed in a polythene beaker containing 30 mL of water. 20 mL conc. HCl and 20 mL conc HNO₃ were added. When all the melt is dissolved the crucible and the lid were taken out of the beaker after repeated washing with water. The solution was allowed to cool to room temperature than 1 g of NaF was added and dissolved by stirring with plastic rod and then the solution was saturated with KCl. The precipitate of K₂SiF₆ was allowed to settle and was filtered through Whatman No. 42 filter paper using polythene funnel. The beaker, rod and the filter paper was washed thoroughly with wash solution. Finally the precipitate along with the filter paper was transferred into polythene beaker containing 25 mL ice-cold wash solution with 2 drops of bromothymol

Table 1.
Chemical analysis

Constituents %	Sample 1	Sample 2	Sample 3
SiO ₂	95.65	98.92	99.44
Al ₂ O ₃	0.58	0.48	0.47
Fe ₂ O ₃	0.03	0.00	0.00
CaO	0.05	0.00	0.00
MgO	0.03	0.01	0.01
Na ₂ O	0.00	0.00	0.00
K ₂ O	0.02	0.01	0.00
TiO ₂	0.05	0.03	0.02
MnO	0.08	0.06	0.05
LOI	3.21	0.17	0.00

blue indicator. The filter paper was teared with the plastic rod. In contact with silicofluoride precipitate, pH of the solution decreases sharply and reaches a fixed value 5.1. At this pH the following equilibrium is established.



The beaker was again kept on the ice bath to keep temperature below 4 °C. The residual free acid was neutralized with N/15 NaOH solution to a blue end point at ice-cold condition. 200 mL of distilled water was boiled in a conical flask with 2 drops HCL (1:4) and 4 drops of BMT. The hot water was neutralized with N/15 NaOH solution to just blue colour. The content of the plastic beaker was transferred slowly into the quartz conical flask containing remaining neutralized water. The beaker was washed with neutralized hot water until the blue colour ceases to change. The flask was heated to boiling and then liberated HF was titrated with standard N/15 NaOH. The end point was indicated by sharp change of yellow to blue via green.

The result of analysis by the prescribed method has been given in Table-I. Several experiments were carried out with sample 1, to determine the exact fusion temperature. It has been observed that if the sample is fused at 550 °C with covering the lid for 15 minutes a good result is obtained. If the fusion temperature is raised above 600 °C, low value is obtained which is due to loss of silica by evaporation. Moreover, after the formation of silicofluoride precipitate, if the temperature is raised above 4°C, a low value is obtained which may be caused by liberation of HF due to hydrolysis reaction.

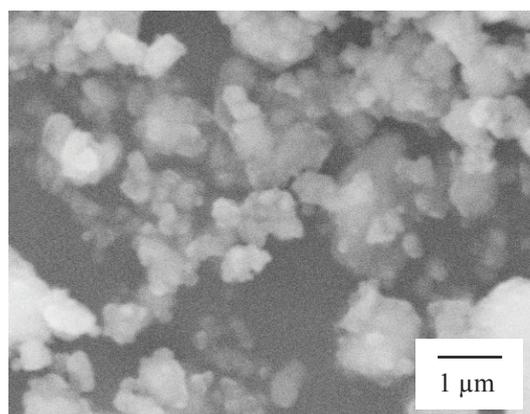
IR Studies

In order to gain better insight into the surface functional groups available on the surface, their IR spectra were recorded. IR spectrum of all the adsorbents showed four intense bands. The sharp bands in range 3380-3454 cm^{-1} attributed to the surface hydroxyl group and chemisorbed water. The band at 1100-1115 cm^{-1} was assigned due to Si-O-Si, -C-O-H stretching and -OH deformation. The peak at about 469 cm^{-1} indicates the presence of Si-H.

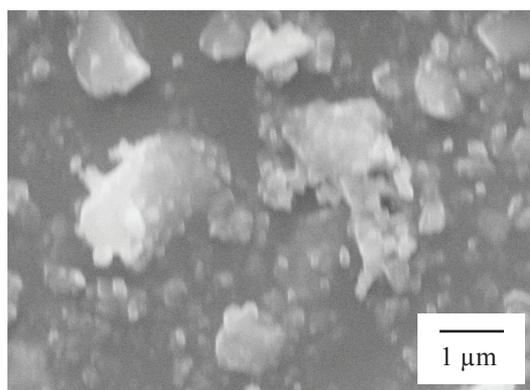
SEM and XRF studies

The scanning electron micrographs (SEM) of the sample 1-3 are shown in the Fig. 1(a), 1(b) and

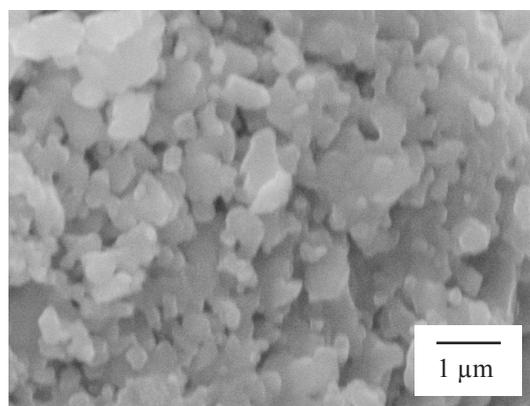
1(c) respectively. The SEM analysis shows that surface morphologies of the silica changes with heat treatment temperature. On chemical treatment rice husk is converted to charcoal with carbon and silica as the main constituents. On sintering at 1000 °C, carbon remained in the structure burned out resulting porous structure (Fig.1).



Sample 1



Sample 2



Sample 3

Fig.1. SEM micrograph of the silica

This is because of the agglomeration of fine carbon particles would results in large voids, which may prevent shrinkage of the structure and consequently cause porosity and giving high surface area. SEM diagram for sample 1 and 2 showing agglomerated particle, but for sample 3, a homogeneous particle size distribution is found. The average particle size and surface area are presented in Table-II. XRD pattern (Fig. not shown) of all the samples show a single hump indicating disordered structure. It seems that X-ray diffraction is mainly due to amorphous silica particles. As the atomic scattering factor for carbon is very small, intervening carbon atoms seem to contribute very little with respect to scattering from silica.

Table 2.
Physical characteristics

Characteristics	Sample 1	Sample 2	Sample 3
Mean particle size (μm)	85	63	44
Surface area (m^2/gm)	194	244	282

Conclusion

It is shown that pure and amorphous silica with high specific surface area can be easily obtained from rice husk. By acid treatment the metallic impurities of rice husk could be removed. Sintering at 1000°C amorphous silica is obtained with high specific surface area. It is observed that with increasing sintering temperature silica content in the sample increases. The products with such small particle size and high surface area can be use with different aims. Determination of exact quantity of silica is also important for analyst to detect its application. The modified volumetric method is found suitable for the determination of exact quantity of silica content in the sample.

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References

- [1] Larrard F., Gorse J.F., Puch C., Mater. Struct 25: 265 (1992).
- [2] Boateng A.A., Skeete D.A., Cem. Concr. Res 301: 139 (2000).
- [3] Hunt L.P., Dismukes J.P., Amick J. A., J. Electrochem.Soc. 131(7) :1683 (1984).
- [4] Banerjee H.D., Sen S.N., Acharya H.N., Mater. Sci.Eng. 52 :173 (1982).
- [5] James J., Rao M.S., Thermochem. Acta 97 :329(1985).
- [6] Nakata Y., Suzuki M., J. Ceram. Soc. Jpn 97 :830(1989).
- [7] Krishnarao R. V., Mahajan Y.R., Kumar T.J., J. Eur. Ceram. Soc. 18 :147(1998).
- [8] Hanna S.B., Mansour N.A.L., Taha A.S., Abd-Allah H.M.A., Br. Ceram. Trans. J. 84 :18(1985).
- [9] Chakrabaerty A., Mishra P., Banerjee H.D., J. Mater. Sci. 23 :21(1988).
- [10] Real C., Alcala M.D., Criado J. M., J. Am. Ceram. Soc. 79 (8) :2012(1996).
- [11] Yalcin N., Sevinc V., Ceram. Int. 27:219(2001).
- [12] Dasgupta S.and Roy S.K., "Chemical analysis of ceramic and allied materials" 1985 P. 38.
- [13] Travers A., Compt.Rend., 185: 893 (1927); Jour.Soc. Glass.Tech., 40 : 512T (1956)
- [14] Louvrier J. and Voinovitch I.A., L'Indust. Ceram., 510 L:243 (1959).
- [15] Kumar S., Sen R. and Sinha B.C. Trans. Ind. Ceram. Soc., 22(1):22. (1963).

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