Synthesis and characterization of nanosilica from rice husk ash by precipitation method for chemically synthesized nanocement

[1] Pattipati Janasree, [2] Meda Kalyan Kumar
[1,2] Department of Chemical Engineering,
JNTUA College of Engineering, Ananthapuramu, Andhra Pradesh, India.

Abstract : Chemically synthesized nanocement is an alternative to ordinary Portland cement avoiding emission of CO_2 into the atmosphere. Nanosilica is an essential ingredient in the preparation of chemically synthesized nanocement. Nanosilica is prepared by precipitation method from rice husk ash, an abundant material available in rice growing states like Andhra Pradesh. Characterization is done using techniques X- ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and Dynamic Light Scattering (DLS).The results of the techniques revealed the particles to be amorphous and irregular in structure. Major chemical constituents are Si, O, and Na. The mean size of particles using DLS is found to be 168 nm. From the characterization results it is concluded that the precipitation method has been successfully used to prepare nanosilica from rice husk ash, suitable for preparation of chemically synthesized nanocement.

***Index Terms* - nanosilica, nanocement, rice husk ash, precipitation, CO_2 emission**

INTRODUCTION

Reduction of CO_2 emission

Currently more research is going on to reduce CO_2 emissions responsible for global warming and climate change. One such effort is replacing the cement with alternative materials such as fly ash, slag, metakaoline etc. This analysis focuses on the chemically synthesized nanocement as an alternative to 'Ordinary Portland Cement'. The chemical synthesis of nanocement is very effective in enhancing the mechanical and physical performance of cementitious material and also controls the CO_2 emission during its production [1, 2]. In the preparation of nanocement, nanosilica produced from rice husk ash (RHA) is used as a precursor.

Rice husk ash as a source for nanosilica

Rice husk is one of the most important agricultural wastes abundantly available in rice-producing countries such as China, India, Indonesia, and Bangladesh. Normally, rice husk is considered as waste, and disposed primarily by natural burning, creating not only air pollution but also liberating fine silica ash, which is toxic. Furthermore, this treatment practice leads to production of very large amount of CO_2 gas released to the atmosphere. Currently rice husk continues to gain growing interest as a potential source of silica [3, 4]. Rice husk is a by-product generated by rice mills. During milling of paddy about 78% of weight is received as rice. Rest 22% of the weight of paddy is received as husk. RHA is produced by burning rice husk under controlled temperatures between 600 to 700°C temperatures for 2-6 hours. Rice husk ash has been reported to be a good pozzolanic material by numerous researchers [5]. After combustion, the organic composition is decomposed and rice husk ash is attained. RHA among the family of agro-wastes is the most silica rich, containing silica 90% to 98% and some amount of metallic impurities.

RHA is a cheap silica source. Due to features such as low cost, low density characteristic, void filling levels, renewable and biodegradable nature, silica has found many applications, such as fillers in composite materials, rubber etc. RHA is used as silica precursor in ceramic materials, such as ceramic pigments and ceramic glazes. RHA as a pozzolanic material with a large amount of amorphous SiO_2 and a large surface area can also be used in production of ultra-high performance cement [8].

Preparation of nanosilica

It is important that the silica in RHA exists in the amorphous state with high surface area. Nanosilica synthesized by the precipitation method resulted particle size of 50 nm [6, 7]. To get the nanosilica, rice husk ash is treated with sodium hydroxide, forming sodium silicate. Sodium silicate is then treated with sulphuric acid to form precipitate [9]. The precipitate is washed with distilled water, dried and ground to obtain the nanosilica. To reduce the cement quantity and to upgrade the characteristics in concrete mixtures, nanosilica is used [10]. Among the various nanomaterials nanotitania, nanoalumina, nanosilica, nanoFe_2O_3, nanozirconia the addition of nanosilica particles (NS) has the possibility to react with calcium hydroxide to develop more strength carrying structure of cement [11].

The nanosilica is prepared by using different chemical methods such as sol–gel synthesis, vapour-phase reaction and thermodecomposition methods. In most of the above methods, nano silica powder is synthesised using chemicals as a precursors. In these methods, it is easy to control size, purity of the material but the initial raw materials are costly. In large scale industrial applications, large quantity and low cost precursor are preferred. Therefore agricultural by-products such as rice husk, rice straw, and plant materials are used to produce silica. Earlier study identified that rice husk can be used for the production of widely applicable and valuable nanosilica [12]. Therefore, it is of great interest to investigate the development of process for pure nanosilica from naturally available raw material rice husk for the preparation of chemically synthesized nanocement [13].

MATERIALS & METHODS

Materials

Rice husk was obtained from a local rice mill and was washed with water. Sodium hydroxide (NaOH), Sulphuric acid (H2SO4) both AR grade purchased from SRL were used.

Experiment

Preparation of rice husk ash

The rice husk, was washed thoroughly with distilled water to remove impurities. The washed rice husk was air-dried at room temperature and then burnt at 700oC for 6 h in a muffle furnace to obtain rice husk ash.

Preparation of sodium silicate solution

Rice husk silica was extracted using an alkali extraction process, adopting the precipitation method. Typical experiment was carried out by transferring 30 g of rice husk ash into a glass beaker containing 500 mL of 3M NaOH solution. The solid RHA was mixed with the sodium hydroxide solution and boiled under reflux for 4 h with vigorous magnetic stirring during the whole reaction process. The temperature of the whole system was maintained at 80oC. The final mixture was allowed to cool down to room temperature. The mixture was filtered to separate the filtrate which contains sodium silicate, while the residue was discharged.

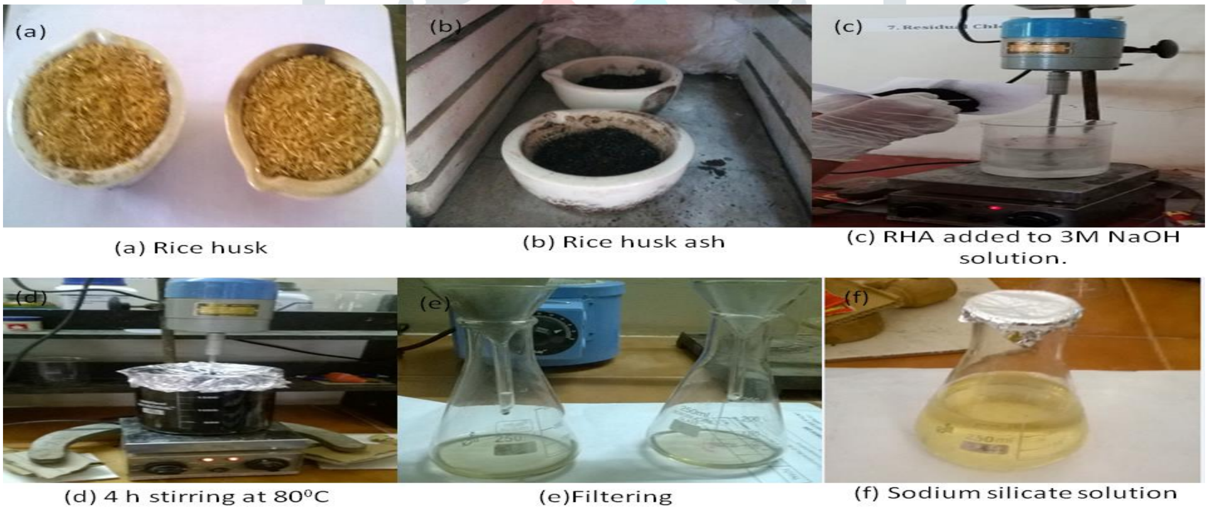

Fig.1. Preparation of sodium silicate solution from rice husk

Precipitation of nanosilica

The pH of the filtrate (sodium silicate solution) was reduced using controlled addition (drop wise) of concentrated sulphuric acid, while being stirred magnetically, to extract the nanosilica precipitate. After repeated washing of precipitate, the solids were collected and dried at room temperature for 72 h. The solids were crushed and ground to powder using high energy ball mill, for obtaining the nanosilica grains. The process of silica dissolution and precipitation is described by the following reactions.

i. $SiO_2 + NaOH \rightarrow Na_2SiO_3 + H_2O$

ii. $Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$

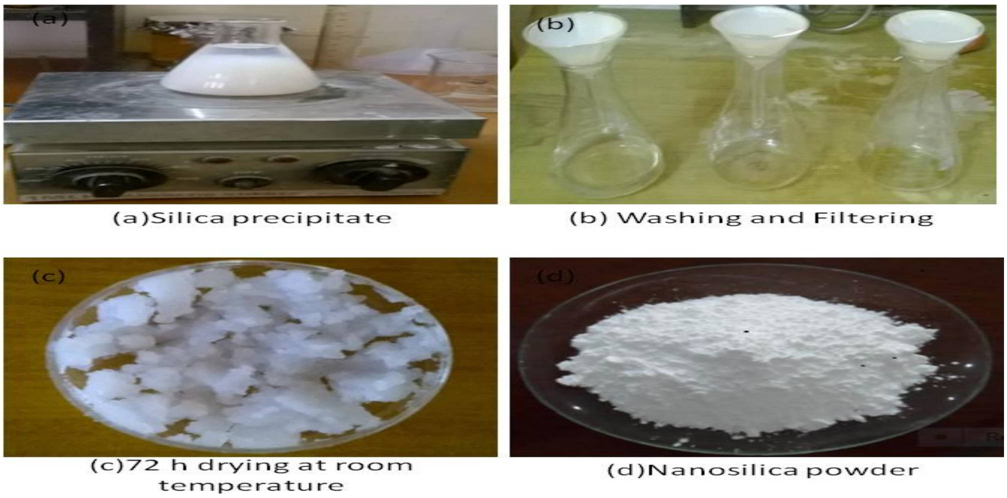

Fig.2.Synthesis of nanosilica by precipitation method

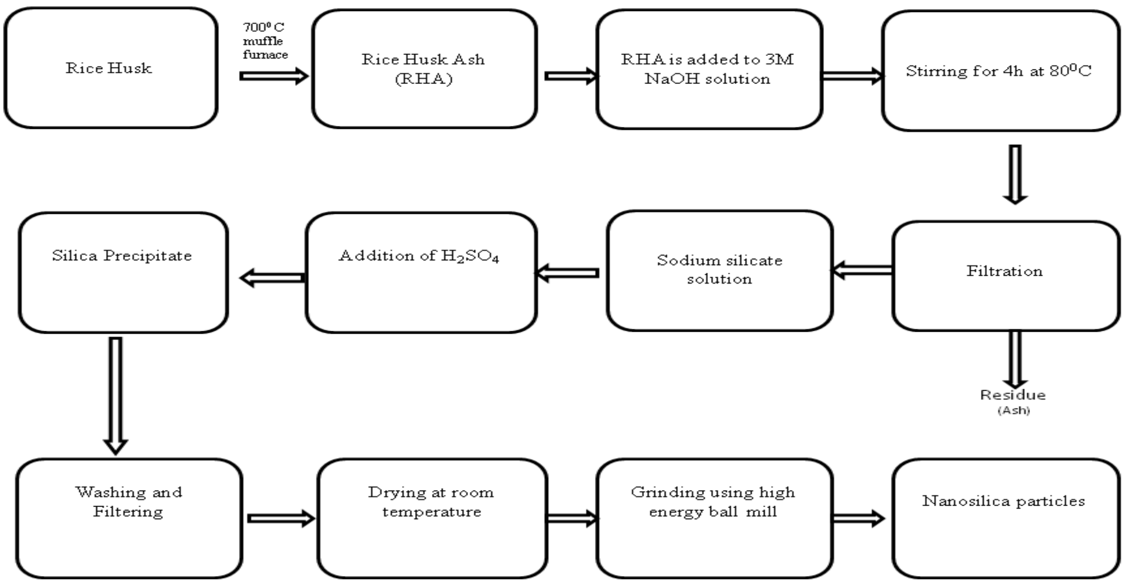

Fig.3. Flowchart for preparation of Nanosilica by precipitation method

Characterization

X-ray diffraction (XRD) analysis of SiO_2 nanoparticles was recorded on a WRD Panalytical XPERT 3 PRO X-Ray diffractometer using Cu-K_α (λ = 1.54060 nm) as the radiation source in the 2θ range of 0° - 100° with a step size 0.005 and a step time of 0.15 s. Scanning electron microscopy (SEM) integrated with EDX was performed at 5.0 kV with magnification 503.58 KX for 20 nm, 201.70 KX for 100 nm, 51.13 KX for 200 nm and 10.75 KX for1 μm scale respectively. Dynamic light scattering was performed with scattered angle 173^0.

RESULTS AND DISCUSSION

X-Ray Diffraction analysis

In order to identify the nature of synthesized nano SiO_2 either it is crystalline or amorphous, X-ray diffractogram (XRD) is used. This method is based on diffraction angle of a certain material. XRD data analysis (Fig.4.) showed that the structure of synthesized nanoparticles was similar to those mentioned in the references [13, 14, and 15]. Strong broad peaks of nanosilica are centered range on ≈ 22-24° SiO_2.The results show that nanosilica is in an amorphous state.

Fig.4. X –Ray Diffractogram of nanosilica.

Field Emission Scanning Electron Microscopy (FESEM) analysis

Surface morphology using 'Field Emission Scanning Electron Microscopy' (Fig.5.) revealed that SiO_2 particles were irregular in shape [16].

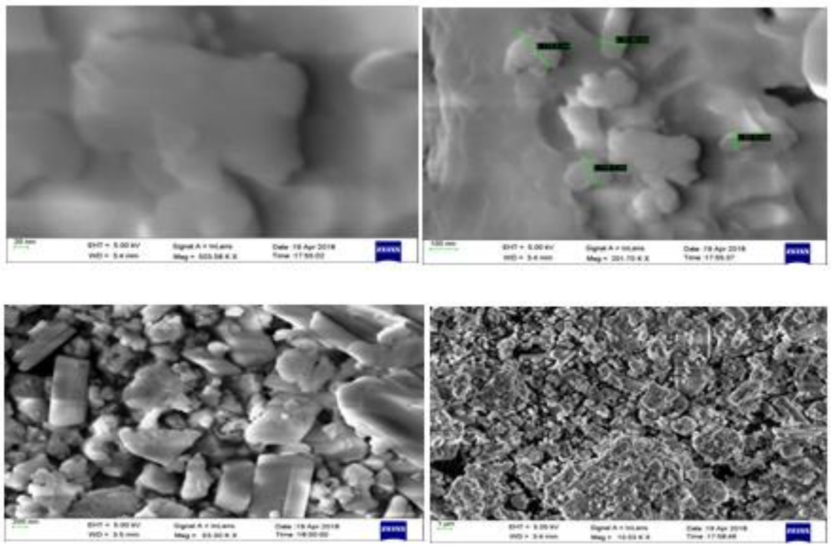

Fig.5. FESEM micrograph of nanosilica

Energy Dispersive X-Ray (EDX) Analysis

Energy Dispersive X-Ray Analysis (Fig.6.) gives elemental composition of synthesized sample. The below figure peaks represents the elemental composition of silica. The spectra contain predominantly the elements of Si, O, Na, C. Both Si and O peaks correspond to the silica. The signals originate from sodium and carbon due to precursor NaOH and carbon coating [16].

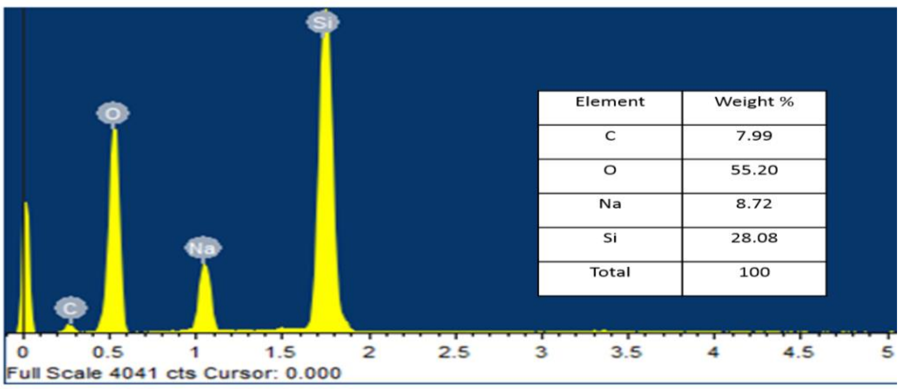

Fig.6. EDX of nanosilica particles.

Dynamic Light Scattering [DLS]

The particle size distribution (Fig.7)of the nanosilica synthesised in this investigation belongs to the range between 6 nm to 10 µm. Maximum particles are in the range of 10-100 nm size. The mean value 168 nm and the mode value 33 nm are observed from results.

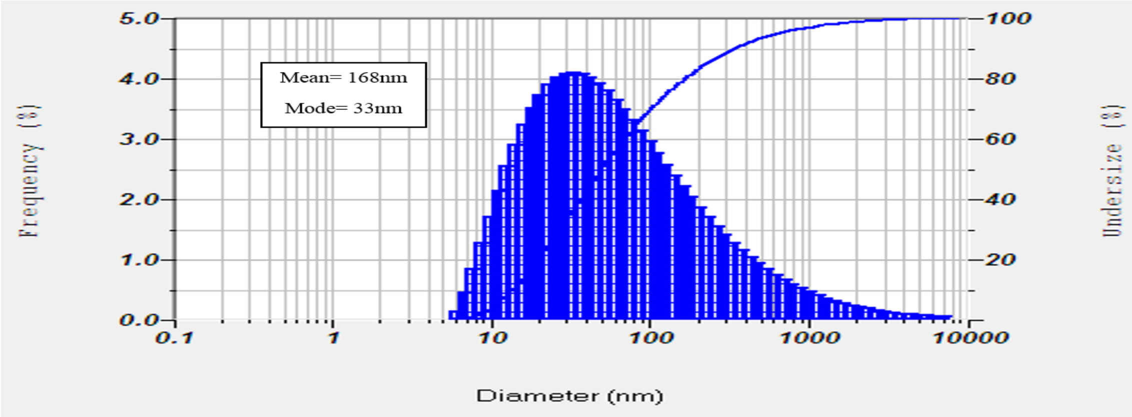

Fig.7. DLS analysis of nanosilica particles

CONCLUSION:

Nanosilica particles 15 g were obtained from 30 g rice husk ash using precipitation method. XRD shows that powder is amorphous. SEM images reveal irregular-shape morphology. Purity of the nanosilica was confirmed by EDX analysis. The average size of the particles is 168 nm as represented by the DLS image. The method is very simple and effective for nanosilica production useful for the chemical synthesis of nanocement.

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