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Nanosilica Extracted from Sand as Corrosion Inhibitor

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Abstract

Silica powder at nanoscale was obtained by alkali fusion route from river-based sand followed by heat treatment. The crushed sand is treated with NaOH then heat treated to obtain silica nanopowder. In order to identify the optimal condition for producing the homogenous silica nanoparticles, the effect of heat treated temperature is investigated. By the analysis of X-ray diffraction, scanning electron microscopy, the silica product obtained was found to be amorphous and the uniformity of the nanosized sample was observed at an average size of 99 nm. The results obtained in the mentioned method prove that the waste sand is one of the best and cheaply available sources that can be used for the production of silica nanoparticles. The synthesized silica nanoparticles show excellent corrosion inhibition efficiency on carbon steel.

Keywords: Silica nanoparticles; Inhibitor efficiency; X-ray diffraction; Morphology; Amorphous.

Introduction

Recently, silicon oxides, commonly named silicas, in their corpuscular form, have become useful materials in various fields because they have new physicochemical properties which do not appear in the corresponding bulk materials. Amorphous precipitated silicas are used as dielectric materials, elastomeric materials, in flat panel displays, sensors, filters for exhaust gasses, adsorbents, separations, biomedicine, drug delivery systems, oil-spill clean-up, heterogeneous catalysts in various chemical reactions and food materials.

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Colloidal silica is a stable dispersion of solid silica particles, has found various applications such as investment casting, semiconductor wafer polishing, coating, textiles, it has also been used as an inorganic binder, a nanosize filler, and as a catalyst precursor [1, 2]. Silica has good properties such as a high specific surface area, high gas absorbability, and high oil absorption sothese properties are added to the coated pigment specifications [3, 4]. It is also one of the most effective chemicals for paper coating due to its high brightness, opacity, porosity and hydrophilicity. The application of these materials, for instance, as fillers in the paper industry may contribute to the fibre-to-fibre bonding, when coated with silica thus improving paper strength [5]. Silica is introduced as nanoparticles with core-shell structure representing a new type of constructional units; such materials enhance physical and chemical properties, thus allowing a broader range of applications compared to the single components [6].There are a wide variety of silica nanoformulations being investigated for biomedical applications [7]. Various methods for the preparation of nanoparticles are employed such as plasma synthesis, chemical vapour deposition, micro emulsion processing, combustion synthesis, sol-gel processing, hydrothermal techniques etc. Recent efforts for the preparation of nanoparticles are focused on controlling size, morphology and surface reactivity of nanoparticles. Sol-gel method has been widely used and a method of choice for the preparation of nanoparticles, as it has several advantages such as synthesis may be carried out at low temperature, desired pH to yield high purity and also the reaction kinetics of the process may be controlled by varying the composition of the reaction mixture [8,9]. A pioneering works in this direction on the synthesis of spherical and monodispersed silica particles were reported by Stober et al. [10]. Silica particles with the size ranging from 5 to 2000nm from aqueous alcohol solutions of silica alkoxides in the presence of ammonia as catalyst (basic condition) have been produced. Following that much contemporary research works describing the synthesis of nano silica particles are indeed evolved from the Stober method. The main advantage of Stober method is the ability to form monodispersed spherical silica particles compared to the acid-catalyzed systems which usually result from gel structures. Preparation of silica from rice husk by researchers has been known internationally [11, 12]. This kind of silica has been shown to be a good material for the synthesis of very pure silicon, silicon nitride, silicon carbide, magnesium silicide, and other applications. The production of reactive nanoscale silica from rice husk is a simple process compared to other conventional production techniques such as vapour phase reaction, sol-gel process, etc. The development of an ultra high strength in cement replacement materials can be done to achieve high mechanical performance by the addition of nanosilica which is extracted from rice husk a waste material. In the same direction of extracting nanosilica from natural waste, present work emphasizes on extraction of silica nanoparticles from river-based natural sand. The

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prepared silica showed interesting nanostructures with excellent corrosion inhibition property.

Experimental

Primary Treatment of Sand

The silica sand was collected from Godavari River, Basar, Telangana State, India. The sand with 30μ particle size and more Glassy like structure is taken, weighed using electronic balance and treated with concentrated HCl for 15 hours. HCl is a strong acid so it can dissolve all impurities and extra elements. Then obtained sand sample is continuously washed with distilled water until the acid is totally removed from the sand and dried in electric hot air oven at 150°C for 1 hour. The final weight of the sand is measured and weight loss of nearly 10% was observed. Sand samples were crushed into powder to form 2μ particle size approximately and then used further.

Secondary Treatment

The synthesis of amorphous silica can be done by alkali fusion route (Fig. 1). In this method, NaOH (a strong base pH-14) is added to above-prepared sand which acts as a bonding agent to separate the silica (SiO_2) from other impurities and to reduce the silica particle size into nanometer. For this sand powder (5g) and NaOH (99%) in pellets form is taken in 1:4ratio and is heat treated at temperature varying from 600°C to 900°C. Silica reacts with NaOH as Equation (1) and forms sodium silicate ($Na_2O.xSiO_2$), a pale blue color solid. Then formed sodium silicate is heated with 250ml of distilled water with continuous stirring on a magnetic stirrer at around 60°C for 2 hours. While stirring, the solution changes into pale yellow color. Now Conc. HCl is added to this yellow solution until the pH reaches to 1-2 and the white colored silicic acid gel is formed as shown by Equation (2). When the pH is coming down from highly basic condition to pH-7 to 8 the total solution will terminate into a loose cheese-like structure, from which one can observe the formation of amorphous silica. The obtained white silicic acid ($Si(OH)_4$) gel is washed continuously with distilled water at least for 10 times until the formed by-product NaCl is totally removed from the solution. Then precipitated silicic acid gel is dried in electric hot air oven at 150°C for 6 hours to obtain silica as shown in Equation (3). After which the sample is weighed in electronic balance to note down the final weight and it was observed to show a weight loss of 76%. This sample is further characterized by using XRD, SEM and EDS.

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$$4NaOH_{(s)} + 2SiO_{2(s)} \rightarrow 2Na_2SiO_{3(s)} + 2H_2O \uparrow \quad (1)$$

$$2Na_2SiO_3 + 4HCl + 2H_2O \rightarrow 4NaCl + 2Si(OH)_4 \downarrow \quad (2)$$

Silicic acid (gel)

$$2Si(OH)_{4(aq)} \rightarrow 2SiO_{2(s)} \downarrow \quad +4H_2O \uparrow \quad (3)$$

Amorphous silica

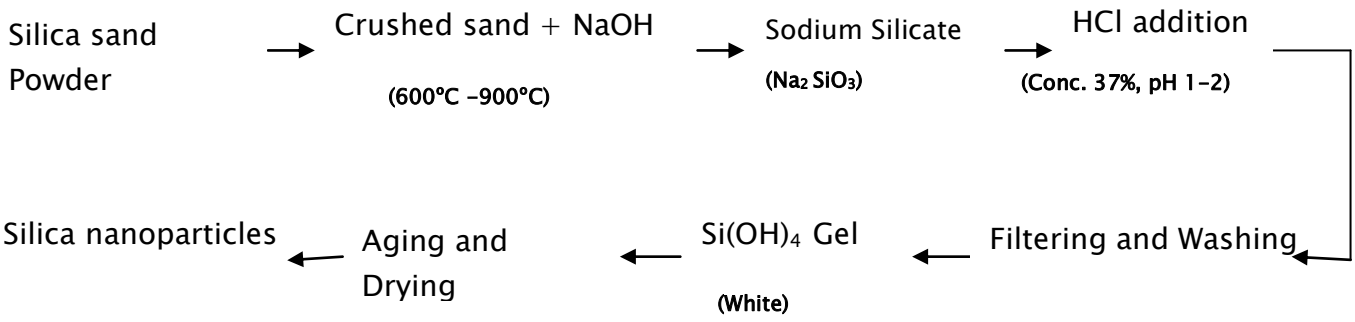

Figure 1. The Alkali-fusion Route to synthesize the Silica Nanoparticles using Heat Treatment (600°C-900°C)

Characterization

The amorphous nature of SiO_2 synthesized was determined by X-ray diffractometer (D8 Discover, Bruker AXS Co. Ltd, Germany) using Cu- Kα radiation λ= 1.54056 Å operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ range from 10° to 90°, with a step size of 0.02°. The particle size and morphology was derived from field emission scanning electron microscope (Carl Zeiss Co. Ltd., Germany) and the elemental composition was obtained from energy dispersive X-ray spectroscopy attached to FESEM (EDX INCA, OXFORD Instruments.).

Corrosion inhibitor efficiency study: Weight loss measurements

Polished specimens were initially weighed in an electronic balance. Five weighed carbon steel samples were taken out of which one is immersed in 40mL of distilled water and other four are immersed in 40mL of 3M NaOH with varying concentrations of nanosilica (0.25, 0.5, 0.75, 1.0 grams respectively). After 124 hours, they are taken out and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and

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reweighed. From the change in weight of specimens the corrosion rate and inhibitor efficiency was calculated using Equation 4 and Equation 5 respectively.

$$\textbf{Corrosion Rate (mpy)} = \frac{534 \times \Delta W}{(A \times T \times D)} \quad (4)$$

ΔW = Loss in weight in mg

A = surface area of the specimen (inch^2)

T = Time in hrs

D = Density (g/cc)

$$\%\textbf{IE} = \left(1 - \frac{CR_1}{CR_0}\right) \times 100 \quad (5)$$

CR_1 = Corrosion rate in presence of nanosilica

CR_0 = Corrosion rate of blank sample

Results and Discussion

SEM micrographs

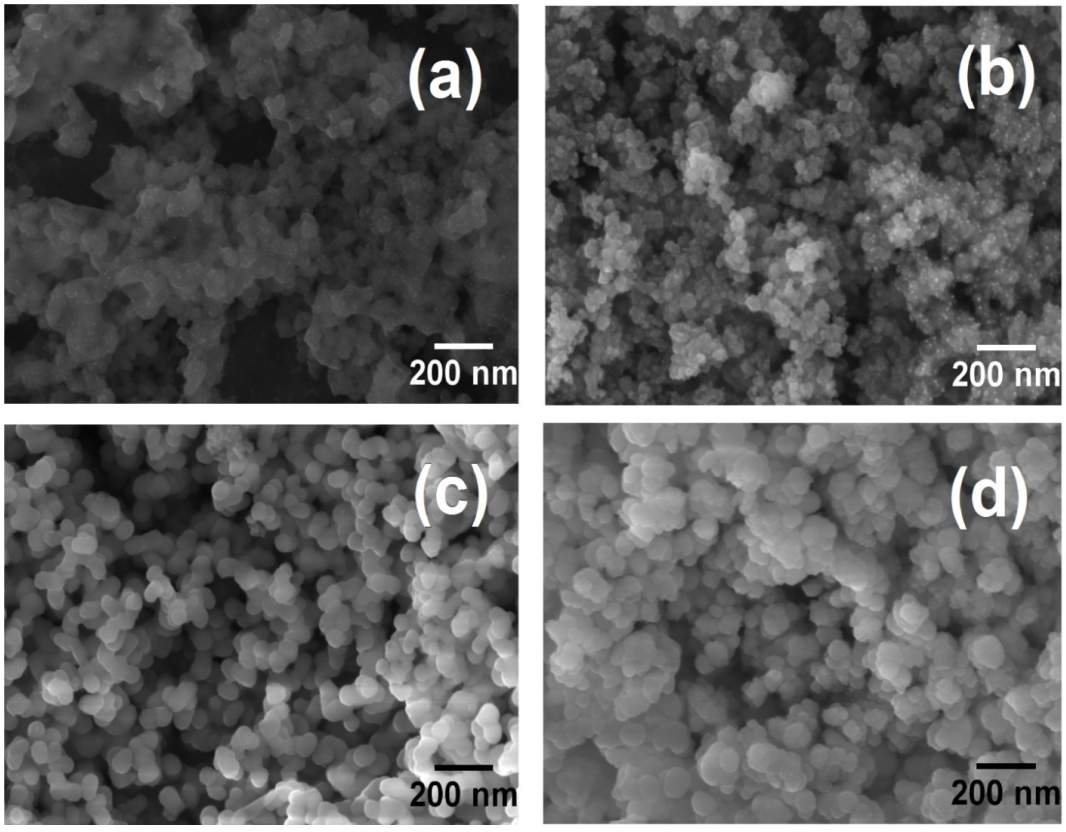

Figure 2. Nanosilica heat treated at (a) 600°C; (b) 700°C; (c) 800°C; (d) 900°C

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Silica nanoparticles were prepared by simple alkali fusion route. Effect of temperature was studied to understand the change in size and morphology of silica nanoparticles. The samples were characterized by SEM to find the morphology and size of silica nanoparticles. SEM micrographs clearly shows that as temperature increases from 600°C to 900°C for same concentration of NaOH say 1:4 ratio (sand: NaOH), the distribution of the size of the particles calculated by imageJ software is shown in table 1 and the mean value clearly shows that as temperature increases the particle size increases. Interestingly it was also observed that the morphology which was small cubes at 600°C were aggregated at 700°C then changed to spherical particles at 800°C which again shows aggregation at 900°C (Fig. 2). Moreover, the SEM images at low temperatures show white dots on the particles clearly which vanish at high temperatures as they get sintered. Nano silica was prepared by other techniques such as using sol-gel process with Tetra ethoxysilane (TEOS) as starting material [13] , extraction of nanosilica from rice husk using sol-gel techniques [14] etc. All these techniques involve a surfactant to reduce the particle size to nano size. This work presents interestingly the synthesis of nanoparticles in a very simple route with fascinating morphologies as observed in Fig. 2.

Table 1. Particle size distribution range and Average Particle size obtained from SEM micrographs

Heat treated Temperature	Particle sizes distribution range (nm)	Average particle size (nm)
600°C	12 to 106	72
700°C	14 to 184	93
800°C	7 to 249	109
800°C	30 to 191	123

Powder XRD

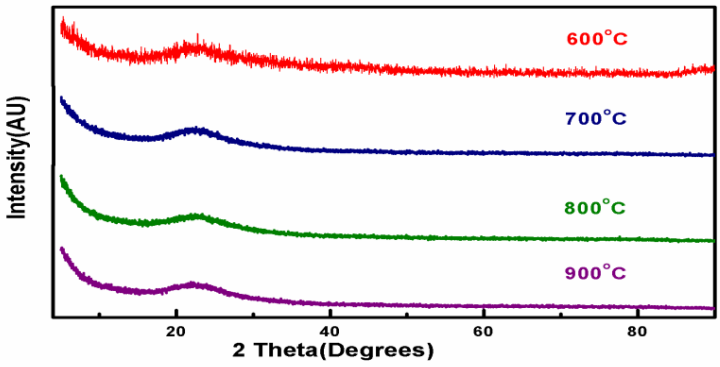

Figure 3. XRD patterns of nanosilica at different temperatures

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In addition X-ray, powder diffraction shows no characteristic peak indicating amorphous nature of all the samples (Figure 3). A very broad peak nearly at 22° may be a characteristic peak of nano silica as reported by Le et al. [14].

Nanosilica as corrosion inhibitor

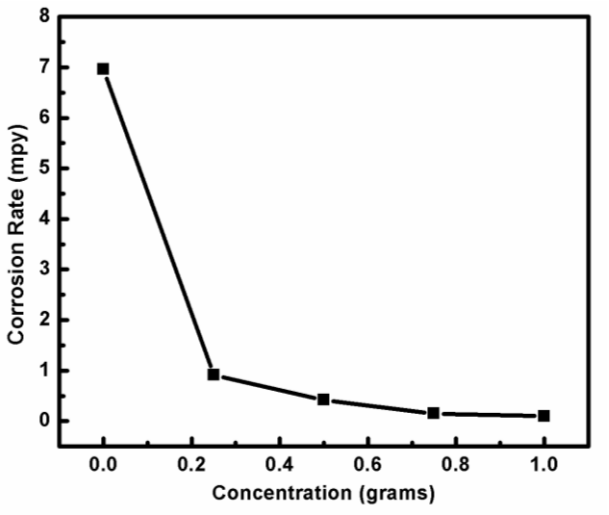

Figure 4. Corrosion Rate Vs Inhibitor Concentration

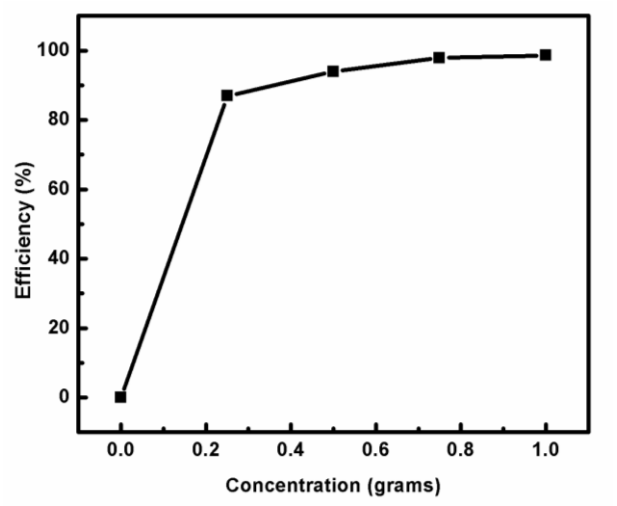

Figure 5. Efficiency Vs Inhibitor Concentration

The results of the gravimetric determination of corrosion of carbon steel in distilled water medium without and with the addition of various concentrations of nanosilica are summarized in Table 2. The corrosion rate of carbon steel decreases and the percentage of inhibition efficiency increases with the concentration of inhibitors. Fig. 4 shows change in corrosion rate with inhibitor concentrations and Fig. 5 depicts the change of Inhibitor Efficiency (%) with concentration of nanosilica. The inhibitor efficiency of nanosilica attained increased from 86.92 to 98.56 (%) when the concentration of inhibitor was increased. These results display the performance of nanosilica extracted from river-based sand as an excellent inhibitor. Even with small concentrations of inhibitor, satisfactory efficiency was obtained.

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Table 2. Corrosion rate and % inhibitor Efficiency at different concentrations of nanosilica

Inhibitor concentration in g	Weight loss in mg	Corrosion rate (mpy)	% Inhibitor efficiency
0	11.4	6.96	-
0.25	1.50	0.91	86.92
0.5	0.70	0.42	93.96
0.75	0.26	0.15	97.84
1.0	0.18	0.1	98.56

Conclusion

Silica nanoparticles were successfully synthesized from the abundant river based sand. A new synthetic method for spherical and block shaped silica nanoparticles using sand as the silica source and the effect of heat treatment temperature was investigated. This method is a simple and effective route for preparing ultrafine powders on a nanometer scale and with a homogeneous particle size distribution. The silica product obtained is amorphous. This leads to the low-cost production of silica nanoparticles for various practical applications such as pollution treatment, nanocomposite materials, etc. Furthermore, the corrosion inhibition property was studied on carbon steels and was found that the nanosilica shows excellent corrosion inhibition efficiency up to 98.56%. So using this source for the production of nanosilica is proved to be one of the best techniques.

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