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Synthesis of nanosilica from silica fume using an acid-base precipitation technique and PVA as a nonionic surfactant

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Abstract

The purpose of the present study was to synthesize and characterize nanosilica from alkali-extraction of silica fume under controlled conditions using poly (vinyl alcohol) (PVA) as a dispersing agent. The dissolution efficiency of silica fume was affected by various factors such as concentration of the reagent, reaction time and temperature. A maximum dissolution efficiency of 91% was achieved at the sodium hydroxide solution concentration of 2.5 M, after areaction time of 30 minutes and at areaction temperature of 80°C. The microstructure and morphology of the obtained nanosilica powder at the optimum conditions were characterized using scanning electron microscopy (SEM). SEM images confirmed the formation of smaller and less agglomerated nanosilica particles due to the existence of the surfactant. Further, the synthesized nanosilica was characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffractometry (XRF) and X-ray diffraction (XRD). The results show that the synthesized nanosilica consisted of pure silica particles.

Keywords: *nanosilica; silica fume; dissolution efficiency; surfactant; PVA.*

1. Introduction

Nanosilica is a basic raw material that has high porosity and surface area, and can be widely used in various industrial applications, such as thixotropic agents, thermal insulators, fillers, adhesives, electronics, ceramics, mechanical materials, and so on [1–3].

Silica that possesses a porous structure and nanoscale particles can be produced using several methods such as sol-gel [4–7], precipitation [8], plasma [9], combustion [10], chemical vapor deposition (CVD) [11], microemulsion [12], microwave heating [13], and so on. In the conventional industrial method of producing silica, sodium carbonate powder reacts with quartz sand after being smelted at a high temperature, as a result of which sodium silicate solution forms.The precipitated silica is obtained from the reaction between sodium silicate solution and sulfuric

acid solution. This method is relatively hazardous to the environment owing to resultant disposal as well as environmental pollution problems, such as carbon dioxide (CO_2), sodium sulfate and waste water. Moreover, a large amount of energy is consumed during the preparation of silica since the reaction occurs at a very high temperature [14]. However, other production methods have limitations, such as the use of high-cost raw materials like tetraethylorthosilicate (TEOS), producing hazardous wastes, consuming relatively large amounts of energy, and limitations related to size and shape [15]. Therefore, it is believed that a cheaper and more environmentally friendly method needs to be found for the synthesis of nanosilica from suitable silicon-containing materials. This will be of great importance.

Using low-cost source materials can significantly reduce the costs of production methods. One such material is silica fume which is also known as microsilica. It is a byproduct of smelting quartz and quartzite in electric arc furnaces of silicon and ferrosilicon alloy at high temperatures. Silica fume, as a rich source of silica, contains about 85 wt% SiO_2, has very fine particles that are smaller than one micrometer, and gives a high level of specific surface area [16,17].

In an aquasol (a dispersion of particles in water), also calleda hydrosol, the excess water molecules interact with the free hydroxyls on the surface of the silica particles, and these particles form big clusters. During the drying process, strong chemical bonds form between particles, and a particle agglomerate appears [18]. This problem may be solved using a suitable surfactant as a dispersing agent to prevent the agglomeration of particles.

Poly (vinyl alcohol) PVA with the chemical formula $[CH_2CH(OH)]_n$ is a nonionic polymeric surfactant which contains a large number of hydroxyl groups per molecule. It is used in many fields including papermaking, textiles, coatings, and in most applications where surface activity is required [19]. Several studies have investigated the use of surfactants such as Poly (vinyl acetate) (PVAc) [20], polyethylene glycol (PEG) [18, 21], sodium dodecyl sulfate (SDS) [22], PVA [23,24], and so on, as dispersing agents in the synthesis of silica nanoparticles. The main objective of this study was to prepare nanosilica particles from silica fume, which is a cost-effective source of silica using an acid-base precipitation technique by adding PVA as a dispersing agent. Further, for the purpose of optimizing the synthesis conditions, the influencing parameters on the dissolution efficiency of silica fume have been discussed.

In the literature, there is no report on the application of silica fume and PVA as a nonionic surfactant to the synthesis of nanosilica using a precipitation technique under optimum conditions. Compared with the so-called conventional industrial method, the proposed method not only reduces the production costs, but also eliminates some of the problems relating to disposal, as well as problems relating to environmental pollution.

2. Materials and methods

2.1. Materials

Silica fume was purchased from Iran Ferroalloy Industries Company. Its chemical composition (in wt%) was SiO_2, 96.12; Al_2O_3, 0.82; K_2O,0.40. The density and specific surface area of the original sample were 0.213 g/cm^3 and 18,000 m^2/kg, respectively. Sodium hydroxide pellets (NaOH, 97%) and sulfuric acid (H_2SO_4, 95–97%) used in the synthesis procedure were of analytical grade and were purchased from Merck Chemical Company. PVA with 99% hydrolysis and an average molecular weight of 88.000 g/mol was purchased from Sigma-Aldrich.

2.2. Preparation of nanosilica

The procedure used for the synthesis of nanosilica from silica fume is shown schematically in Figure 1. One gram of silica fume is added to a reactor containing sodium hydroxide solution with a known concentration. The contents are constantly stirred at a certain temperature for a particular length of time until all the silica was dissolved and sodium silicate solution is obtained (Eq. 1). After filtration, the precipitation of nanosilica was carried out by neutralizing the produced sodium silicate solution with an acid. The sodium silicate solution was stirred at a constant rate, and a 2.5 M sulfuric acid

solution was added gradually so that silica gel formed at a constant pH value of 8–9 (Eq. 2). Before the gelation of hydrosol, a small amount of 1% PVA solution was added to the hydrosol. The precipitated silica gel was then washed with distilled water several times until the filtrate was free from solute salts, such as sodium sulfate, left over from the neutralization stage. The gel was dried at 80°C for 48 h and then the collected solids were calcined to remove the dispersing agent's matrix. Finally, the residue was ground using a mortar and was screened through a sieve to obtain silica nanoparticles.

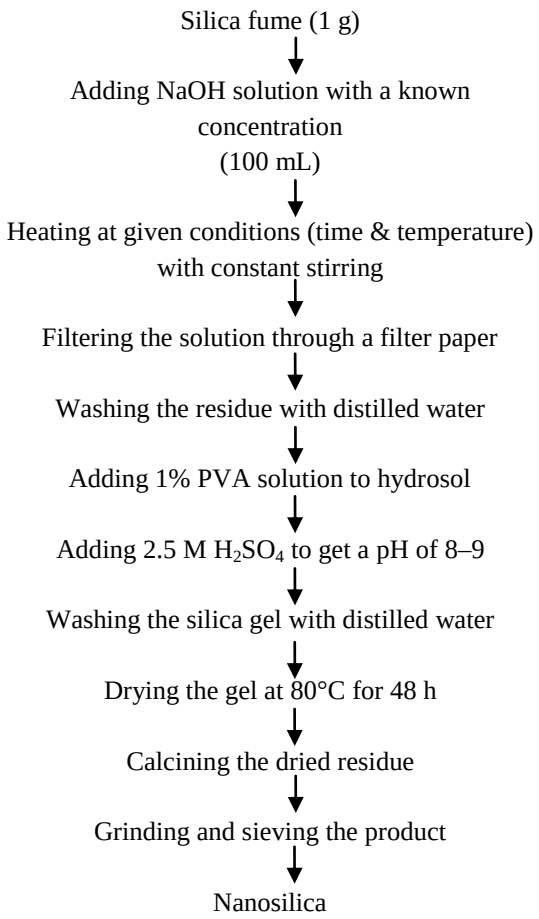

Fig. 1. Flow diagram of the procedure used to synthesize nanosilica from silica fume

$$SiO_2\,(Silica\,fume) + 2\,NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O \quad (2)$$

2.3. Characterization

The nanosilica obtained at optimum conditions was subjected to different characterizations. Result of dynamic light scattering (DLS) analysisis in the form of particle size distribution in terms of light scattering intensity. It can be converted into the particle size distribution in terms of the number of particles which is more useful for comparison purposes [25]. The particle size distribution of samples was determined by DLS measurements (Malvern, ZEN 3600 Zetasizer) with a 633 nm He-Ne laser source and a detection angle of 90°. For the observation of the morphology of nanosilica particles, the sample was characterized by a scanning electron microscope (SEM) (Philips, XL-30) employed at an operating voltage of 30 kV. To prepare the sample for SEM analysis, a known amount of the produced nanosilica powder was suspended in ethanol, and then a drop of the sample was spread on a glass slide and was allowed to dry completely at room temperature (25°C). Finally,the sample was coated with a thin layer of gold to prevent buildup of charge. In order to recognize the functional groups of the produced nanosilica, Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum, RX 1) was performed by the KBrpellet method. The chemical composition of the produced nanosilica was determined by X-ray fluorescence (XRF) analysis (Philips, PW1480). For phase identification of the produced nanosilica, X-ray diffractometry (XRD) analysis (JEOL, JDX-8030) was carried out employing Cu-Kα radiation at an operating voltage and current of 30 kV and 20 mA, respectively.

3. Results and discussion

3.1. Dissolution efficiency

The process of silica fume dissolution was carried out using alkali leaching by sodium hydroxide solution which is described through Eq. (1). The effect of three reaction variables, that is, concentration of sodium hydroxide solution, reaction time and reaction temperature, on the dissolution efficiency of silica fume in sodium hydroxide solution was determined. These variables were controlled at different

levels as follows: the concentrations of sodium hydroxide solution were 1, 2, 2.5 and 3 M; reaction temperatures were 60, 70, 80 and 90°C; reaction times were 10, 20, 30 and 40 minutes. To determine the effect of the abovementioned factors on the dissolution efficiency of silica fume and find the optimum experimental conditions, one factor at a time was varied while the other factors were held constant.

3.1.1. Effect of concentration of sodium hydroxide solution

The dissolution efficiency of silica fume affected by different concentrations of sodium hydroxide solution is shown in Figure 2. In order to investigate the effect of the concentration of sodium hydroxide solution on the dissolution efficiency of silica fume, the reaction was performed at 80°C for 30 minutes with the concentration of sodium hydroxide solution varying from 1 to 3 M. According to Eq. (1), the increase in the concentration of sodium hydroxide solution is propitious for the dissolution of silica fume. The dissolution efficiency of silica fume, therefore, increased very steeply with increasing sodium hydroxide concentration. A maximum dissolution efficiency of 91% was achieved at the concentration of 2.5 M. The increase in dissolution efficiency of silica fume with sodium hydroxide concentration can be explained as follows: reactions (3), (4), (5), (6) and (7) occurred in the alkali dissolution process of silica fume (Eq. 1). The increase in the concentration of OH^- due to the increase in sodium hydroxide concentration led to more silica being leached out from silica fume. Thus, the content of SiO_3^{2-} increased, and this accelerated reactions (5) and (6) so that the dissolution efficiency of silica fume increased. However, as Figure 2 shows, further increase in the concentration of sodium hydroxide beyond 2.5 M did not result in any increase in the dissolution efficiency of silica fume.

$$NaOH + H_2O \rightarrow Na^+ + OH^- + H_2O \quad (3)$$

$$2OH^- + SiO_2 \rightarrow SiO_3^{2-} + H_2O \quad (4)$$

$$SiO_3^{2-} + H_2O \rightarrow OH^- + HSiO_3^- \quad (5)$$

$$HSiO_3^- + H_2O \rightarrow OH^- + H_2SiO_3 \quad (6)$$

$$NaOH + SiO_2 + H_2O \rightarrow Na^+ + OH^- + H_2SiO_3 \quad (7)$$

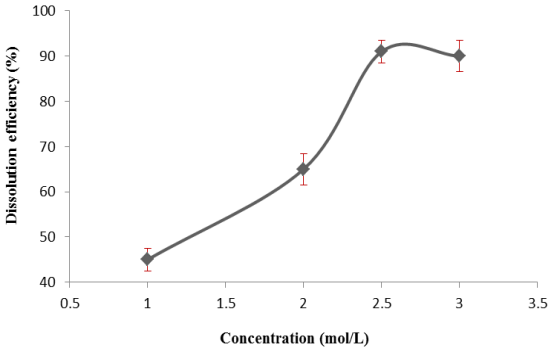

Fig. 2. Effect of sodium hydroxide concentration on the dissolution efficiency of silica fume at reaction temperature and time of 80°C and 30 minutes, respectively

3.1.2. Effect of reaction time

Figure 3 demonstrates the effect of reaction time on the dissolution efficiency of silica fume. To find the effect of reaction time on the dissolution efficiency of silica fume, the reaction time was varied from 10 to 40 minutes, while sodium hydroxide concentration and reaction temperature were held constant at 2.5 M and 80°C, respectively. As can be seen, there was a rising trend in the dissolution efficiency of silica fume with a much steeper slope, lasting up to 30 minutes of reaction time. The maximum value of the dissolution efficiency of silica fume was about 91% which was achieved after 30 minutes of reaction. However, no significant increase in the dissolution efficiency of silica fume was observed at reaction times beyond 30 minutes. The influence of reaction time on the dissolution efficiency of silica fume might be explained by the fact that silica fume needs at least 30 minutes to dissolve, so 30 minutes was confirmed to be the optimal reaction time.

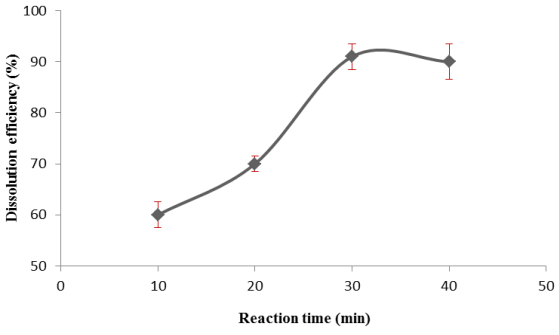

Fig. 3. Effect of reaction time on the dissolution efficiency of silica fume at sodium hydroxide concentration and reaction temperature of 2.5 M and 80°C, respectively

3.1.3. Effect of reaction temperature

In order to investigate the influence of reaction temperature on the dissolution efficiency of silica fume, the sodium hydroxide solution with the concentration of 2.5 M was mixed with silica fume and then the mixture was heated up to different temperatures ranging from 60 to 90°C for 30 minutes. As can be seen in Figure 4, when the other factors were held constant, the dissolution efficiency of silica fume increased sharply with an increase in the reaction temperature from 60 to 80°C, and reached the maximum value of 91% at the reaction temperature of 80°C. Further increase in reaction temperature above 80°C showed no more increase in the dissolution efficiency. The influence of reaction temperature on the dissolution efficiency of silica fume might be explained by the principle of reaction kinetics. Reaction (1) is an endothermic reaction and is accelerated at higher temperatures, thereby increasing the dissolution efficiency.

3.2. Particle size distribution analysis

Figure 5 demonstrates the particle size distribution of nanosilica prepared by the precipitation method at optimum conditions with and without 1% PVA in terms of light scattering intensity and number of particles. As can be seen, 27.3% of the particles (in terms of number) in the nanosilica produced in the absence of 1% PVA demonstrated sizes below 30 nm. It is obvious that the particle size decreased by the addition of 1% PVA so that 83.5% (in terms of number) of particles demonstrated sizes smaller than 30 nm. For a better comparison, DLS results of the samples are reported in Table 1. The minimum particle size, average diameter, and maximum particle size of the samples are obtained from the diagram of particle size distribution in terms of number of particles. As can be seen, with the addition of 1% PVA, the minimum particle size, average diameter, and maximum particle size of the sample decreased from 15.69, 39.57 and 141.8 nm to 10.10, 23.06 and 78.82 nm, respectively.

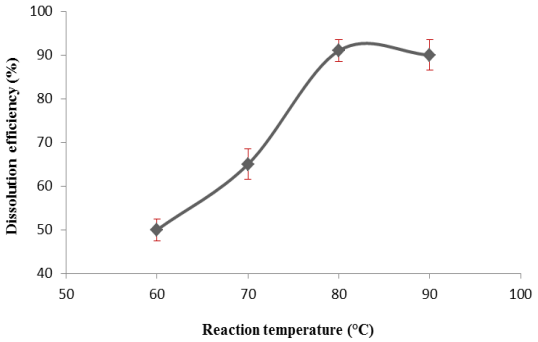

Fig. 4. Effect of reaction temperature on the dissolution efficiency of silica fume at sodium hydroxide concentration and reaction time of 2.5 M and 30 minutes, respectively

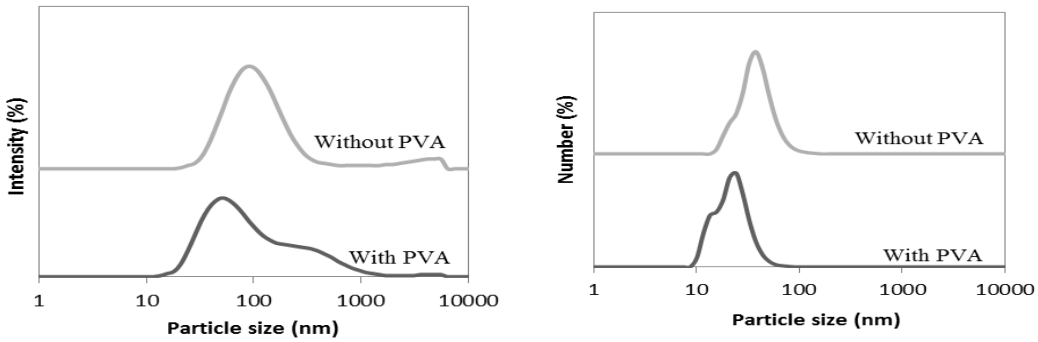

Fig. 5. Particle size distribution of nanosilica produced by precipitation method with and without 1% PVA in terms of the number of particles (right side) and light scattering intensity (left side)

Table 1. Particle size of nanosilica produced by the precipitation method with and without 1% PVA

Sample	Min size (nm)	Average diameter (nm)	Max size (nm)
Without PVA	15.69	39.57	141.8
With 1% PVA	10.10	23.06	78.82

3.3. SEM analysis

The SEM micrographs of the synthesized nanosilica at the optimum conditions with and without 1% PVA are shown in Figure 6a and b, respectively. As can be seen, SEM analysis indicated that the size of the produced silica particles with and without 1% PVA was in the nanometer range, but the micrographs showed that the nanosilica prepared by the addition of 1% PVA had a lower particle size in comparison with the nanosilica produced without PVA. This confirms that PVA had a strong effect on the reduction of particle size. As Figure 6b represents, in the absence of PVA, the produced nanosilica contained larger particles with a higher tendency for agglomeration and cluster production. The SEM image of the nanosilica prepared with 1% PVA (Fig. 6a), however, shows that the presence of 1% PVA resulted in the formation of smaller and less agglomerated particles which were freely dispersed on the surface. Therefore, the use of PVA as a nonionic surfactant had a strong effect on the size of the nanosilica particles. Additionally, it can effectively prevent the aggregation of silica nanoparticles as well as cluster formation because PVA molecules can be absorbed on the surface of the formed silica nanoparticles through hydrogen bonds to form space steric effect, which prevents further growth of the nanoparticles. According to the theory of homogenous nucleation, the nucleation rate increases with decreasing surface tension. Surfactants decrease the surface tension (or interfacial tension) between the surface and water, so, their presence in solution effectively increases the nucleation rate, and the particle size of product is decreased [18,26]. Addition of PVA increases the nucleation rate (a high number of formed nuclei are obtained), and decreases the growth rate of formed nuclei of the produced nanosilica particles. This means that PVA, as a surfactant, plays a significant role in the formation of smaller and less agglomerated nanosilica particles, modifies the particle surface, and prevents more agglomeration of particles. This observation confirms the discussion held earlier about DLS results. Moreover, the relatively small and big clusters, as seen in SEM images, could also be a result of drying and calcination processes which cause the formation of strong chemical bonds between neighboring particles, and then the hard agglomerates appear. Furthermore, the last stage, in which the silica powder was ground, reduced the size of the large particles and produced small particles of irregular shapes. The SEM images, therefore, represent clusters of very small nano-sized particles.

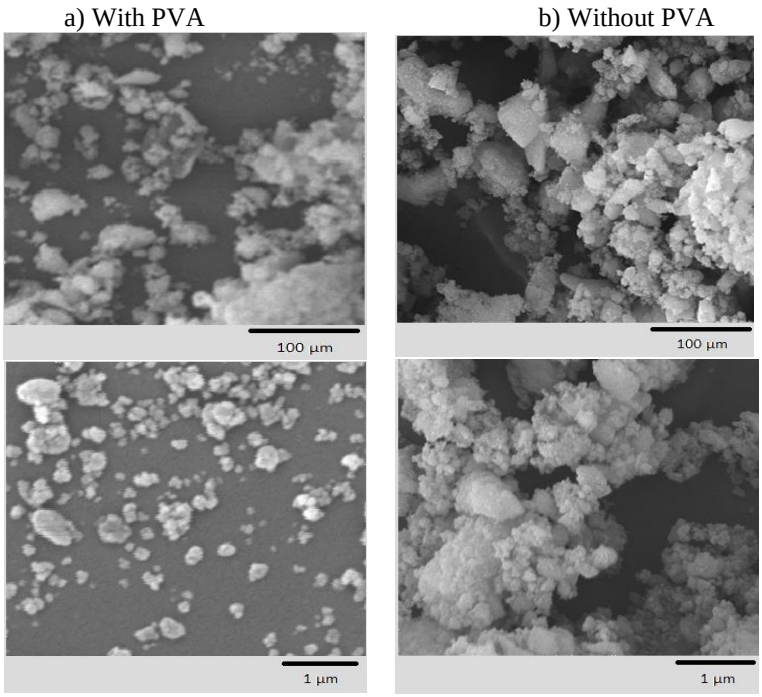

Fig. 6. SEM micrographs of nanosilica particles produced by the precipitation method a) with and b) without 1% PVA

3.4. FTIR spectroscopy analysis

FTIR results of nanosilica prepared by the precipitation method under optimum conditions in the presence of PVA as a nonionic surfactant are shown in Figure 7. The broad band in the range of 2800–3750 cm^{-1} is due to the stretching vibration of the O–H bond. The absorption band at 3450 $cm^{-1}$is attributed to the H–O–H stretching, while the band at 1647 cm^{-1} is believed to be due to the bending vibration of the water molecules. The vibration of oxygen atom in silicon atom in the asymmetric, symmetric and the bending modes of Si–O–Si band appeared at 1090, 785 and 465cm^{-1}, respectively [27–29]. The FTIR results confirmed that the produced sample consisted of pure silica.

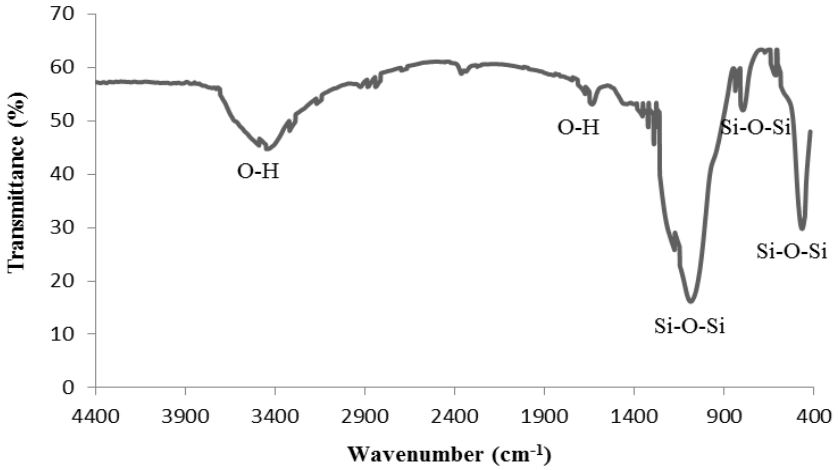

Fig. 7. FTIR spectrum of nanosilica produced by the precipitation method in the presence of 1% PVA as a surfactant

3.5. X-ray fluorescence analysis

The chemical composition of nanosilica prepared by the precipitation method at optimum conditions in the presence of PVA as a nonionic surfactant is reported in Table 2. As can be seen, with a silica content of 99.87%, the product can be considered as relatively highly pure nanosilica.

Table 2. Chemical composition of nanosilica produced by the precipitation method in the presence of 1% PVA as a surfactant

Composition	Value (wt. %)
SiO_2	99.87
Al_2O_3	0.02

3.6. X-ray diffraction analysis

Figure 8 represents the X-ray diffraction pattern of the nanosilica prepared by the precipitation method under optimum conditions in the presence of PVA as a nonionic surfactant. As can be seen, the pattern shows no peak, and the broad rise centered at 2θ angle of about 22.3° is a known typical characteristic of silica. The absence of any ordered crystalline structure confirmed that the produced nanosilica was completely amorphous in nature [27–29].

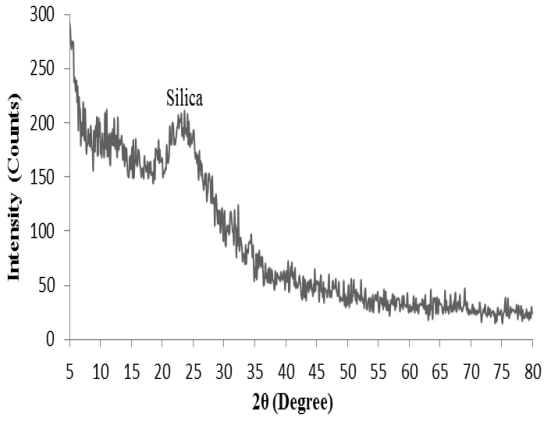

Fig. 8. X-ray diffraction pattern of nanosilica produced by the precipitation method in the presence of 1% PVA as a surfactant

4. Conclusions

Nanosilica can be successfully prepared from alkali-extraction of silica fume under controlled conditions using 1% PVA as a dispersing agent. The optimum conditions under which preparation and synthesis of

silica powder were determined so that a maximum dissolution efficiency of silica fume equal to 91% was achieved at the sodium hydroxide solution concentration of 2.5 M, after a reaction time of 30 minutes, and at a temperature of 80°C. Studies by SEM analysis confirmed that by adding 1% PVA, smaller and less agglomerated nanosilica particles can be produced. FTIR, XRF and XRD results showed that the synthesized nanosilica consisted of pure silica particles.

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