A Facile Method for Production of Amorphous Silica from Perlite under Microwave Irradiation

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ABSTRACT

The objective of this study was to develop a method to produce amorphous silica from perlite under microwave irradiation and to determine the influence of different NaOH concentration, microwave irradiation time and temperature on the percentage yield of SiO2 content in the obtained amorphous silica. The whole process was divided into three steps:- (i) alkali solubilisation of perlite (ii) subsequent gel formation and (iii) acid dissolution. The synthesized materials were characterized by XRF, BET surface area, XRD, FTIR and SEM-EDS techniques. The maximum percentage yield of SiO2 (94.48%) content was extracted by 4 N NaOH at 90 °C for 15 min. The specific surface area of synthesized AS was found to be ~104 m²/g. EDS analysis indicated that silicon was the most abundant element present in AS. The XRD pattern and FTIR data supported the increment in amorphous nature and hydrogen bonded silanol and siloxane groups in AS respectively as compared with raw perlite. The results show that this novel preparation procedure provides an easy pathway to produce amorphous silica with high SiO2 content from perlite, solid waste, according to specification.

Keywords
Amorphous silica, Affecting factors, Microwave irradiation, Perlite

1. INTRODUCTION

Perlite is a naturally occurring amorphous, hydrated volcanic glass formed through the secondary alteration of obsidian by the incorporation of water into the glass silica structure and can be an economically viable for production of silica gels and powders. The estimated worldwide reserves of perlite are estimated about 700 million tonnes [1]. The use of silica from the perlite is a major concern of research interest. Their approach may be classified into two categories: (a) purification or modification of perlite to produce highly pure silicon and (b) silica compounds utilization as an economic source of silica for the cement industry, lightweight construction products, abrasives and absorbents [2].

Perlite is rich in silica that is a cost effective raw material for dried silica gel (SG) and amorphous silica (AS) production. SG is the amorphous (non-crystalline) form of SiO2 which contains three-dimensional network or aggregated silica particles of colloidal dimension and is classified as aquagel (pores filled with water), xerogel (aqueous phase in the pores is removed by evaporation) or aerogel (solvent is removed by supercritical extraction) while AS is a fine powder form with high surface area obtained by coagulation of particles from aqueous solution under the influence of appropriate electrolyte concentration [3]. Both materials have many potential applications, such as reinforced filler, an adsorbent, a catalyst host, for chromatograph packing columns, in cosmetics, in vegetable oil refining, in pharmaceuticals, in paint and coating etc. Commercially, SG and AS are produced from tetraethylorthosilicate through sol-gel process [4] or from the fusion of quartz sand with soda ash in a furnace at high temperature (>1300 °C) [5]. But these techniques are very expensive and energy intensive. Recently, SG and AS have been synthesized from various types of biomass such as rice husk ash [6], rice hull ash [7] and corn cob ash [8] etc. Critical economic and environmental situations of the current days encourage companies and researchers to develop and improve technologies intended to reduce or minimize solid wastes. As a consequence, much effort has been expended in different areas. Therefore, it would be advantageous to develop a simple, economic, time and energy efficient method for the production SG and AS from perlite under microwave heating, thereby utilizing solid waste for an economically value-added product.

Microwave irradiation (MW), a non-classical heating technique has now become an indispensable part of all fields of synthetic chemistry. Green, economic, efficient heating, drastic reduction in reaction time, providing phase purity with high yields under milder reaction condition and high reproducibility like characteristics has made it a promising tool for the synthesis various organic transformations. MW irradiation causes internal heating (in core volumetric heating) by directly coupling with the
molecules of the substrate of reaction, leading to rapid increase in temperature for consuming time and energy [9]. In recent years, synthesis of various types of silica materials such as SBA-15, MCM-41, organosilica and metal modified MCM-41 under microwave heating has also attracted attention due to fast response rate, low energy consumption and the product of uniform size [10]. MW can heat up substances even in Teflon plastic containers which avoid corrosion of reactors due to leaching of strong base. The MW equipment offers an immediate incline to desired temperature and distributes heat homogeneously giving rise to high quality materials [11].

In this context, the use of MW heating for preparation of AS from perlite is proposed. The effects of various parameters such as different concentrations of NaOH solutions, microwave irradiation time and reaction temperature are investigated. AS production from perlite alleviates the solid waste disposal problem and creates a commercially viable value-added product.

2. EXPERIMENTAL

A. Materials and Apparatus
Perlite (SiO$_2$+Al$_2$O$_3$ >70%) was collected from Indica Chemical Industries Pvt. Ltd., Kotdwar, India. All chemicals such as NaOH (99%), H$_2$SO$_4$ (98%) were purchased from S.D. Fine Chem. Ltd., India. The SG and AS preparation are carried out in MW synthesis system made by CEM, USA (Model - Discover) which can adjust its power within the range of 0-300 W (Figure 1).

B. Preparation of AS from Perlite
The whole process as indicated in Scheme-1 is divided into three steps:

(i) Alkali solubilisation of perlite
Raw perlite (RP) was thoroughly washed with distilled water to remove adhering soil, dust and then dried at 110 °C for 12 h. After that, it was calcined at 800 °C for 3 h and name as thermally activated perlite (TAP). 5 g of TAP was added to various concentrations of NaOH solution (1, 2, 3 and 4 N) in open vessel system of CEM MW reactor using round bottomed flask made of Pyrex glass attached with air condenser to produce sodium silicate solution. Then mixture was heated under MW irradiation at 150 W for different time and alkali concentration with high stirring mode to obtain best results. The solution was filtered through Whatman No. 41 filter paper and was washed with 15 ml of de-ionized water. Later the filtrate and washing were allowed to cool to room temperature.

(ii) Preparation of silica gel
In the gelation process, the sodium silicate solution was titrated with 5 N H$_2$SO$_4$ under constant stirring. The pH of the solution was monitored and the titration was stopped at pH 7 to produce SG. The soft gel was aged for 5 h. After aging, the gel was gently broken by adding 30 ml of deionized water to make slurry. Now, the slurry was washed by vacuum filtration using distilled water to remove sodium sulfate followed by drying in a vacuum oven at 80 °C for 12 h and ground into dried SG.

(iii) Synthesis of amorphous silica (AS)
For producing AS, the dried SG was heated with 15 ml of 1 N HCl solution by MW heating at 90 °C for 10 min at 150 W and then washed repeatedly using deionised water to make it acid free. Now, the obtained AS was dried at 110 °C for 12 h.

In order to compare the effect of heating methods same experiment was performed in oil bath under conventional heating maintaining similar reaction conditions as kept under MW heating.

C. Regeneration
Regeneration is the step where calcium hydroxide reacts with sodium sulphate to form calcium sulphate and sodium hydroxide. As per the reported procedure, NaOH is regenerated up to 90 %. The regenerated NaOH solution is used for digestion of the fresh perlite [12]. The obtained calcium sulphate can be used for other laboratory work.

Figure 1. Microwave Synthesis System
**D. Characterization Techniques**

The chemical components of the samples were analyzed by XRF spectrometer (Philips PW 1606). The BET surface area was measured by N₂ adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA 1000e surface area analyzer. Powder XRD studies were carried out by using (Philips X’pert) analytical diffractometer with monochromatic CuKα radiation (k = 1.54056 Å) in a 2θ range of 0° -80°. The particle size of the samples was determined from Mastersizer 3000 laser diffraction particle size analyzer manufactured by Malvern Instruments Ltd. FTIR study of the samples was done using FTIR spectrometer (Alpha-T model, Bruker, Germany) by mixing the sample with KBr pellet mode (in 1:20 wt. ratio) in the range of 4000-400 cm⁻¹. The detailed imaging information about the morphology and surface texture of the sample was provided by SEM (Model - JEOL JSM 5600).

3. **RESULT AND DISCUSSION**

**A. COMPARISON BETWEEN CONVENTIONAL v/S MW HEATING AND EFFECT OF NaOH CONCENTRATION**

Table-1 presents the yield percentage of silica obtained from MW heating in MW reactor and conventional heating in oil bath at various concentrations of NaOH solution (1, 2, 3 and 4 N) which indicates that the concentration of NaOH solution positively affects the % yield of SiO₂ in AS. It has been found that for 4 N NaOH concentration, MW heating for 15 min at 90 °C yielded more SiO₂ in AS (94.48%) whereas at same conditions, the effect of conventional heating showed a quite low yield (87.61%) of product. It has been found that for every NaOH concentration, due to in core volumetric MW heating of materials is produced more silica than conventional heating [13].

<table>
<thead>
<tr>
<th>Concentrations of NaOH solution (N)</th>
<th>Yield of SiO₂ (%) under microwave heating</th>
<th>Yield of SiO₂ (%) under conventional heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N</td>
<td>59.08</td>
<td>47.37</td>
</tr>
<tr>
<td>2 N</td>
<td>73.76</td>
<td>64.06</td>
</tr>
<tr>
<td>3 N</td>
<td>88.96</td>
<td>79.13</td>
</tr>
<tr>
<td>4 N</td>
<td>94.48</td>
<td>87.61</td>
</tr>
</tbody>
</table>

Optimized conditions: Temperature = 90 °C, time = 15 min, power = 150 W

**Figure 2. % Yield of silica in AS obtained as function of concentration of NaOH solution and MW irradiation time**

**E. Effect of MW Irradiation Time**

Exposure time to MW is one of determining factors of AS production. Figure 2 represents a directly proportional relationship of % yield of SiO₂ in AS obtained with MW irradiation time. Increase in MW irradiation time from 5 to 15 min along with concentration of NaOH (1 N to 4 N) solution produced better results. MW irradiation for 15 min using concentration of 4 N NaOH solution produced 94.48% yield of silica which the highest amongst all combinations. On further increasing MW irradiation time and alkali concentration no change in AS amount was observed.
(ii) Effect of Temperature
Figure 3 clearly shows effect of temperature on the % yield of SiO$_2$ in AS. On increasing temperature from 50 to 90 °C, the yield is continuously increased from 40.64 to 94.48%. MW irradiation for 15 min at 90 °C generated maximum yield percentage of silica content.

![Figure 3. Effect of temperature on % yield of silica in AS](image)

B. Characterization of AS
Prior to its use as a raw material, the components of perlite were characterized by XRF (in wt.%): SiO$_2$ (73.9%), Al$_2$O$_3$ (12.6%), Na$_2$O (4.7%), K$_2$O (4.6%), ZnO (0.8%), Fe$_2$O$_3$ (0.6%), TiO$_2$ (0.1%), and trace elements (2.7%). RP contains 73.9 wt.% silica with 5 m$^2$/g surface area and 3.20 µm average particle diameter while TAP possesses 74.3 wt.% silica content with 4 m$^2$/g surface area. Quantitative analysis of the components indicates the obtained AS contains white fine solid with 94.48% yield of SiO$_2$ having ~104 m$^2$/g specific surface area in the range of 500 nm - 0.6 µm particle size. EDS spectra of RP and AS are also shown in Figure 4 indicating the presence of high amount of Si content in AS as compared with RP. Loss on ignition (LOI) is determined by heating a certain weighed quantity of perlite in muffle furnace at 800°C for 3 h. The LOI amount was 4.1 wt. % which corresponds to the removal of moisture and coexisting unburned carbon from sample [14].

![Figure 4. EDS spectra of (a) RP (b) AS](image)

The images of wet SG and AS obtained from perlite are shown in Figure 5.

![Figure 5. Images of (a) Wet SG (b) AS](image)

XRD patterns of RP, TAP, and prepared AS are shown in Figure 6 (a-c) which indicates the hump in the 2θ ranging from 10 to 35º indicating disordered structure, due to AS
particles [15]. A lack of sharp, defined peaks in RP and AS exhibits non-crystalline or amorphous material while TAP exhibits more highly ordered structure along with single crystalline peak at 2θ = 27.59º due the presence of tridymite (polymorphs of quartz) phase (JCPDS No.: 42-1401) [16]. The presence of strong broad peaks in AS suggests more characteristics of amorphous SiO₂ as compared with RP.

FTIR spectroscopic tool is used to identify the key functional groups indicating structural changes in the samples (Figure 7.a-c). A broad band in the range of 3670-3000 cm⁻¹ responsible for the isolated and surface -OH groups of -Si-OH whereas the band at 1630 cm⁻¹ assigned to the bending mode (ν₃OH) of coordinated water [17]. The results indicates that the intensity of these peaks is decreased after calcination whereas is increased after silica extraction. The predominant absorbance peak between 1200 and 1050 cm⁻¹ is associated with the Si-O-Si asymmetric band stretching vibration and the corresponding symmetric stretch at ~802 cm⁻¹ [18]. The intense peak in the range of 470-450 cm⁻¹ is attributed to the Si-O asymmetric bending vibration of Si-O-Si bond. After thermal activation and silica extraction, the intensity of all these peaks is shifted towards higher wave number [19]. AS is exhibited a relatively strong peak at about 817 cm⁻¹ and it can be distinguished from the band of crystalline silicate [20]. The presence of more pronounced Si-O-Si bending vibrations at 473 cm⁻¹ confirms the highly condensed silica network in AS spectra (Figure 7c) [21].

In Figure 8 (a-d), the SEM image of RP (Figure 8a & b) indicates irregular shaped crumbled porous particles with broken or ragged edges [22]. The morphology of TAP (Figure 8c) is less irregular due to evaporation of water from the perlite whereas the SEM micrograph of AS (Figure 8d) demonstrates globular shaped highly porous gelatinous particles of different shapes and sizes in agglomerated form. Such type of large gelatinous mass is due to the presence of amorphous silica gel skeleton [23].

C. Surface chemistry of AS

The surface properties of AS, which is considered to be an oxide adsorbent, in many cases depend on the presence of different types of silanol groups. Surface OH groups are subdivided as following groups and are present on the surface of AS in Figure 9 (a-d): (a) isolated free (single silanols), -SiOH (b) geminal free (geminal silanols or silanediols), -Si(OH)₂ (c) vicinal, or bridged, or OH groups bound through the hydrogen bond (H-bonded single silanols, H-bonded geminals, and their H bonded combinations) (d) surface siloxane groups -Si-O-Si bridges with oxygen atoms on the surface. At last, there is structurally bound water inside the silica skeleton and very fine ultra micropores, d<1 nm (d is the pore diameter), i.e. internal silanol groups [24].
4. CONCLUSIONS

A rapid, simple and energy efficient method has been developed to produce AS from perlite using microwave heating by alkali solubilisation and subsequent acid treatment. Compared with conventional heating method at the same reaction time and temperature, MW heating at 90 °C for 15 min gave a higher percentage yield of AS (94.48%) using 4 N NaOH solution. The study revealed that the obtained AS was found in agglomerated form with ~104 m²/g specific surface area. The used chemicals can be regenerated making it an environmentally benign, cost effective and atom efficient process and finds a novel route to utilize abundant waste perlite in future.

5. ACKNOWLEDGEMENT

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6. REFERENCES


